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ABSTRACT

This publication was produced as a teaching tool for college chemistry. The book is a text for a computer-based unit on the chemistry of acid-base titrations, and is designed for use with FORTRAN or BASIC computer systems, and with a programmable electronic calculator, in a variety of educational settings. The text attempts to present computer programs that are relatively free of reliance on specialized large computer systems programs. The case-study approach presented is highly research and laboratory oriented. Similar subject matter is conventionally taught in most introductory college chemistry courses, but this text material attempts greater depth of instruction through utilization of the computational resources of a computer. (Author/BT)

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Final Report

Project No. 1-A-032
Grant No. OEG-1-71-0012(509)

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CASE STUDIES IN SYSTEMS CHEMISTRY

September 1973

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
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ABSTRACT

The 223-page book, Case Studies in Systems Chemistry: Carboxylic Acid Equilibria, was written, published, and distributed for evaluation as a teaching tool for college chemistry. The book is a text for a computer-based unit on the chemistry of acid-base titrations, and is designed for use with FORTRAN or BASIC computer systems, and with a programmable electronic calculator, in a variety of educational settings. The text is novel in that it attempts to present computer programs that are relatively free of reliance on specialized large computer systems, programs that can be used by individual students in an open-ended manner. This case-study approach is highly laboratory oriented, with a strong research flavor. Similar subject matter is conventionally taught in most introductory college chemistry courses, but this text material permits significantly greater depth of instruction through utilization of the computational resources of a computer.

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George Fleck

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INTRODUCTION

Collegiate instruction in chemical equilibrium and chemical kinetics, the two broad areas of systems chemistry, has been limited in sophistication by the formidable barrier imposed by the repetitive, time-consuming, and boring arithmetic required for comparing data from experiments with predictions of theory. Comparison of data and theory--a central aspect of the appreciation of science as well as a critical aspect of the learning of science--has thus traditionally been given scant attention in introductory college courses dealing with the subject matter of systems chemistry. The wide availability of computers and computer terminals on college campuses has vastly expanded possibilities for exploration of the relationships between laboratory data and theory in systems chemistry, although these possibilities have not yet been exploited. This research project was designed to make available, to both instructors and students, resources needed for utilization of their available computer facilities for college-level instruction in systems chemistry.

Work has progressed in the development of case studies in several areas of systems chemistry, with open-ended descriptions of how computers can be used to facilitate confrontation of student data and the predictions of student-formulated models. A detailed case study in the field of the solution chemistry of acid-base equilibria, appropriate for instruction in an honors section of general chemistry, has been developed as a prototype for other similar text materials projected for coupled equilibria, kinetics, and simultaneous kinetics and equilibria. The complete case study, entitled Carboxylic Acid Equilibria, is submitted as a portion of this final report.

Of strong interest to the investigator has been the presentation of this material in forms applicable to a wide range of computer systems. The case study includes programs written especially for an IBM 1130 system with a plotter, using FORTRAN language, and also related programs written especially for a remote typewriter terminal,

using BASIC language. A program for a Wang 700 series programmable calculator is also included, but our efforts to use such small computers has been disappointing and we do not feel that continued work with programming our Wang 700 or our Olivetti P602 is warranted.

The most important aspect of this research is to alert chemical educators to the new possibilities for teaching what has become a classical subject in general chemistry, analytical chemistry, and physical chemistry. The investigator presented a talk on systems chemistry (see Appendix A) to the New England Association of Chemistry Teachers at their August 1972 meeting, and copies of this talk were distributed to all participants at the 1972 Mount Holyoke Conference on Chemical Education sponsored by the Division of Chemical Education, American Chemical Society. It was announced at these meetings that materials being prepared under this grant would become available during the following year, and could be sent to chemistry teachers upon request.

METHODS

An effective way of demonstrating to teachers of chemistry that a new approach to teaching can be used is to present examples of how it is being used. Likewise, one effective way of showing students how to use a technique is to show it being used, and then ask the student to use the technique in a different but closely related manner. For both reasons, the case study approach has been utilized in this research to provide examples of the use of computers to facilitate the comparison of models and data.

Each computer program is illustrative of a wide variety of similar programs, so that the program need not be followed as a recipe, but can be varied and extended by the student. The programs of the case study are meant to open new vistas, not to exhaust possibilities. A wide range of programs utilizing small desk-top programmable electronic calculators were investigated, with detailed programming attempted with an Olivetti P602 and a Wang 700. One Wang

program is presented in the completed case study, but our efforts with four experienced student programmers and our attempts at stimulating student usage has been disappointing and generally negative. Workable programs for these calculators can be written, but there is an inherent lack of flexibility that inhibits student experimentation with these programs. We have found great enthusiasm for the IBM 1130 programs, particularly with graphical plotter output, and good response to the BASIC programs, contrasting markedly with the responses to the smaller and less versatile equipment.

The original programs were written by the students, in many cases, and many modifications of the programs have been suggested by students. The materials of the case study have been tested by classroom-laboratory use in a college general chemistry course for students with strong science preparation, and in an independent study project by a secondary school senior who was completing a second year of chemistry. Most of the students involved in formulation and testing of this material are girls, and almost all are science majors.

The completed case study, Carboxylic Acid Equilibria, has been sent to 30 interested high school and college teachers who have expressed interest in this research, and some suggestions have been received. Corrections and changes arising from their comments will be incorporated in a set of revision sheets that are to be incorporated in the case study in June 1974. Preliminary responses indicate that the computer programs are indeed usable in computer installations other than the Smith College facilities.

RESULTS

The case study begins with a detailed statement of its performance objectives. Three general objectives are stated, followed by a list of specific objectives written in behavioral terms. The investigator has used this case study for teaching a unit in general chemistry, and has evaluated student performance in terms of the ability to meet the stated general objectives. Such student evaluation

is highly satisfactory with an honors-pass-fail (or its equivalent) grading system. The performance tends to be either full achievement or failure, and the investigator sends students with a performance of 'failure' back to the text, lab, and computer for further work. Mediocre work gets equated with failure, and the middle range of grades gets eliminated. The acceptance of such an evaluation scheme probably carries with it a rejection of a bell-shaped distribution of grades.

The case study is an integrated discussion of theory and methods of treating laboratory data. Computer programming details are introduced as needed. The approach is intended to appear highly pragmatic: methods are introduced whenever there is a need. The goal set before the student is the arranging of meaningful confrontations between data and theory.

Emphasis is placed on model building and on simulation of these models. Students are reminded that a computer gives a novice chemist power to test models that was unavailable to researchers in former decades. Students are encouraged to test assertions that appear in older research articles, as well as assertions made by textbooks, teachers, and this case study. Some teachers may find this open approach threatening, as indeed may some students. But the approach offers an opportunity for students to become liberated from reliance on textbook dogma, and to test important ideas for themselves.

Distinction is made repeatedly between macroscopic and microscopic descriptions of chemical systems, emphasizing that macroscopic descriptions are phenomenological and therefore potentially accessible in terms of experimental observables, whereas microscopic descriptions are necessarily made in terms of theories and thus are accessible only in terms of models. Perhaps the discussions add motivation for the students to achieve facility with simulation techniques, for simulation of models provides an easy method of dealing with microscopic descriptions.

The chemical literature contains vast numbers of research reports dealing with acid-base equilibria with only a few containing as much

detailed quantitative analysis as in this case study. There is thus a reservoir of material in the journals for use in teaching about (and in learning about) the equilibria involving carboxylic acids. Early in the case study (on page 61), there appears a listing of bibliographical sources providing entry for a student into the primary research literature. Additional comments are made throughout the text to lead the student to the library.

The initial computer programs are presented in FORTRAN language, with much of the output to be obtained with a plotter. This is by far the most satisfactory method that has been employed by the investigator. However, adequate results can also be obtained using a time-sharing terminal and employing BASIC language, and several appropriate BASIC programs are presented, beginning with page 90. In every case, effort is made to show a program that "works", but at the same time to encourage the student to adapt that program to the particular specialized needs of the moment.

In teaching this material, the investigator has repeatedly found that students miss many important aspects of both theory and experiment when they do a single experiment with a monoprotic acid. Thus repetition (by titrating a diprotic acid and interpreting that new data) of the whole procedure has a great deal of pedogogical value. Happily, there are many significant features that are new to the diprotic acid case, thus adding some additional interest. The new features center largely about the use of both macroscopic equilibrium constants and microscopic equilibrium constants to describe the same chemical system, and the possibility of having alternative but indistinguishable descriptions of the same system. These features of acid-base equilibria are explored in Chapter 2. Finally, in Chapter 3, polyprotic acid equilibria is introduced in a research context, leaving many possibilities open for the inquiring student and the imaginative teacher.

CONCLUSIONS

It is clear that computer use by students in an introductory general chemistry course can be used to integrate laboratory and classroom, as evidenced by the accompanying textual materials and by their successful use in the investigator's classes. It is the judgment of the investigator that satisfactory evaluation of student performance can be made by using the three general objectives stated at the beginning of the case study. We feel that computer systems comparable to the IBM 1130 with plotter provide flexibility and performance that is completely adequate for the instruction envisioned with this case study, but that further efforts to utilize programmable calculators such as the Wang 700 or the Olivetti P602 are not warranted. Undoubtedly there should be continuing efforts to increase the portability and transferability of computer programs, and other writers should be encouraged to develop better ways of writing programs that can be run on a variety of different computers with a minimum of editing.

The completed case study is evidence that the availability of computing facilities for students can change the substantive content of introductory chemistry courses. The wide distribution of such case studies can be an aid to stimulating similar activity on many campuses, and to exchanging curriculum information between teachers. The case study approach also provides a medium for self study in which a student, with modest laboratory equipment and access to a computer, can learn a substantial amount of science without requiring extensive interaction with an instructor.

Appendix A
New England Association of Chemistry Teachers::August 16, 197?

SYSTEMS CHEMISTRY: PUTTING IT ALL TOGETHER

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Humpty Dumpty sat on a wall
Humpty Dumpty had a great fall;
All the king's horses
And all the king's men
Couldn't put Humpty Dumpty back together again.

Poor Humpty Dumpty got taken apart rather violently. It's easy to smash an egg. With some practice, an egg can be disassembled with more finesse. The art of separating yolk and white is not so hard, unless you insist on using just one hand. And with some more sophisticated techniques, the egg can be separated with finer resolution and a variety of pure compounds can be isolated from an egg. To take apart an egg — even to take apart an egg and separate it into many of its constituent compounds — is a straightforward task. But clearly more than a king's command is needed to put it all back together again.

So it is with descriptions of an egg. Analysis—the description of an egg in terms of its constituents — is straightforward. We can find out what is in the egg, and we can characterize each of the components in terms of its molecular structure. But synthesis — explaining how the molecular constituents function together as a system to create a Plymouth Rock chick — is an intellectual task of considerably greater magnitude. Whether literally or figuratively, it is a whole lot easier to take an egg apart than to put it back together again.

There is a lot to be learned about things by taking them apart. The search for the ultimate parts and pieces of things and stuff was a driving force in transforming alchemy into chemistry. When earth, air, fire, and water were replaced by scores of chemical elements, chemistry had become an analytical science. And when

the elements had been taken apart and found to be made of electrons, protons, and neutrons, part of chemistry had almost become physics. An enticing goal for many chemists has been to talk about the world in terms of simpler and simpler models, and in the process to cut up chemical reality into smaller and smaller pieces.

Yet the rise of chemistry during the past hundred years as a significant force in our society has not appeared to the lay observer to be due to progress in identifying elements, nor to the insights of quantum mechanics, nor to the ability to determine molecular structures, nor to the ability to make refined chemical analyses. Layman, physician, businessman, homemaker, soldier, and politician have seen and felt the impact of chemistry in the twentieth century in terms of a host of new materials put together by the chemists: fabrics, drugs, plastics, explosives, fertilizers, and construction materials. There is private fun in taking things apart, but there is public reward in putting things together, especially for building — that is, in synthesizing — things new and useful.

As we look to the future, we can see new chemical challenges. Design and synthesis of new materials will continue to be important. Society will demand from chemistry new fuels, new fabrics, and new foods at low cost and in abundance, without regard to constraints imposed by thermodynamics. Society will ask chemistry for ways to perform miracles in waste disposal, air and water purification, and instant drug therapy for cancer, heart diseases, and olf age. In a world rapidly moving toward a confrontation with the limits of readily available natural resources, many of the material expectations of society may be found to be unrealistic or unattainable, and chemistry may soon be called upon to help delineate the limits of the chemically-possible exploitation of this planet. Increasingly, chemists may expect to be dealing with more complicated and less well defined chemical systems: the various eco systems, for example, and living organisms, for another. Chemists

will also find themselves talking to economists, politicians, voters, and consumers, trying to explain to this public the limitations placed on chemical systems by the realities of basic physical laws.

In the relationships of chemistry with society, the future will require increasing understanding of complex chemical systems. Chemists will need to know what to expect when lots of interacting molecules get put together. Chemical education should begin now to provide students with the intellectual tools required for coping with complex systems.

TAKING IT APART, VERSUS PUTTING IT TOGETHER: IMPLICATIONS FOR THE CHEMISTRY CURRICULUM

The word system occupies a central place in the teaching of physical chemistry, and the word is commonly used in all areas of chemistry to denote the mixture of chemicals being studied in an experiment. The need is to make the concept of system an open-ended concept, capable of being extended by the student to systems of greater and greater complexity. There needs to be explicit consideration of the ways in which sub-systems combine, for seldom are the properties of a chemical system the simple sum of its parts. There needs to be exploration of the advantages and disadvantages of the phenomenological description of a system, and of the relationships between macroscopic and microscopic variables and models in describing systems. Finally, there needs to be an awareness throughout chemistry that students should be reminded that the real world is made of chemical systems, few of which are understood, many of which need to be understood.

We began to make substantial progress in getting students involved, at the freshman level, with systems chemistry when an IBM 1130 computer became available on campus. For our teaching of solution equilibria and kinetics, access to a computer with a plotter revolutionized our approach. The mathematics has shifted from calculus to arithmetic and simple algebra. The lab and classroom have come closer together, as the computer has

facilitated a teaching strategy in which students confront their experimental data with predictions of their models. By giving the students the powerful tool of computer simulation of a model, the role of the teacher has changed; since the students have the tools to challenge ideas and models presented by the instructor, it is possible to have students and instructor joining forces in an active pursuit of models that are faithful to good experimental data. Finally, the use of simulation techniques means that the students can discover and verify certain properties of systems, without having to accept textbook dogma. We find that realistic small research-type projects are quite appropriate at the college freshman level, at least in small classes with well-prepared students.

Systems chemistry, when taught with the support of computer facilities and a well-staffed laboratory, can enter the chemistry curriculum in various ways. We are struggling with the appropriate places where these concepts ought to be taught. They can be taught very early in a student's career, at the point where we usually teach stoichiometry and titrations. It can come at the point where we usually talk about entropy and free energy. It can wait until senior year, and be used as an integrating course to help put it all together for a student. For the remainder of this discussion, I wish to dwell on the substance of the concepts that need to be taught, without necessarily implying the courses where the concepts might be introduced or reinforced.

CONCEPTS OF SYSTEMS CHEMISTRY

LEVELS OF CONSTRAINT ON A DYNAMIC CHEMICAL SYSTEM. Every reacting system, given a constant environment, is predestined to a particular evolution and a particular equilibrium state. In the absence of an adequate reaction mechanism, few predictions can be made about the initial time-course of the system. The passage of time, though, places constraints on any reacting system. As time goes by, less information is needed to formulate a description of the further evolution of the system. By the same

token, less information about the system is available from data obtained from a system close to equilibrium.

A generally-reacting system can be described from time-zero to time-infinity by postulating a reaction mechanism, and writing a mathematical model that includes a set of mass-action rate equations. If values of the rate constants are known, the system can be simulated by approximating the derivatives in the rate equations by ratios of small differences, and the time-dependence calculated by repetitive arithmetic via a process that is quite appropriate for computer computations. Experimental data can be used to evaluate rate constants, but experiments must be carefully designed for that purpose.

For a complicated mechanism, the early time phase may be categorized as "transient behavior" and ignored, so that attention may be focused on the later stages of the reaction. For any system that can be characterized by mass-action rate equations, eventually all transient behavior passes by, and the final approach to equilibrium is a simple, exponential, first-order relaxation. With some systems, the reaction all (or virtually all) the way from time zero proceeds by one or more first-order relaxations. The time-constant for a relaxation (a macroscopic rate constant) is a function of all the microscopic rate constants of the mechanism. For a complicated system, the approach to equilibrium in a final relaxation is described by a single number. This is a great simplification for macroscopic or phenomenological description. The situation renders hopeless, however, the prospect of gaining detailed mechanistic information about a complicated reaction from data obtained near equilibrium.

Often, but not always, a system may react in such a way so that after an initial transient phase, some of the components may be in a steady-state. Then just a few chemical species are being transformed from reactant to product, while other species have concentrations that are time-invariant. Steady-state systems can be described with fewer variables, but again steady-state rate data

yield less information, than a generally-reacting system. Most biological systems are in steady-states. It would seem that general analysis of steady-state systems must be an important part of a systematic study of systems chemistry.

Finally, there is the equilibrium state. A system that is actually at equilibrium has reacted as far as it can react. Such a system can be described with the minimum number of variables. However, the cost of obtaining this simplicity of macroscopic description is that equilibrium experimental data has essentially no information content regarding mechanisms of reaction.

STABILITY OF A REACTING SYSTEM. Many thermodynamicists speak with assurance when they say that no reacting system overshoots equilibrium, that entropy always increases during a reaction, and that the driving force for achievement of the equilibrium state is the derivative of the free energy with respect to the degree of advancement. Each of these statements may well be true, if properly applied and if properly qualified. Yet apparent contradictions abound. The concentration of an intermediate often overshoots its equilibrium value during the transient phase of a reaction. Sustained oscillations have been observed in several reacting systems.

Thus it is especially instructive to explore some of these general statements about the one-way nature of the approach to equilibrium and the stability of the equilibrium state. A computer simulation is an ideal method for the student to conduct this exploration. Along with the output of concentration versus time, one can calculate entropy and free energy versus time. One can in fact look at entropy and free energy of individual species, as well as for the system as a whole. A student should then formulate some of the general criteria for reacting systems in terms that can be defended on the basis of simulations of reaction mechanisms.

Most elementary chemical reactions have inherent stability because of negative feedback built into the form of the mass-action equations. Some chain reactions appear to lack this stability,

and it is instructive to pinpoint where stability is lost, and how it can be restored. Such considerations of stability are very important in talking about control in a living organism, where steady-state concentrations are regulated by molecular control processes that need to be understood. Using simulation methods, an undergraduate student can subject some of the qualitative ideas that appear in the biochemical literature to some critical tests. The concept of self-regulated dynamic stability is really quite appealing.

STRUCTURE WITHIN A REACTING SYSTEM. Homogeneous solutions are convenient media for performing reaction-rate studies in the laboratory. Homogeneous systems are also particularly amenable to modelling with mass-action rate equations. However, there is evidence that suggests that some types of interesting reactions cannot occur in a strictly homogeneous medium. Certainly, a living cell is a structured medium, and many of the special properties of a cell derive from this structure. There is continuing interest in ways in which an initially homogeneous solution, or gas, or gel can achieve structure. It is not enough to divide the world into homogeneous and heterogeneous media, for the criteria for structure are probably quite subtle. The dynamic stability of non-uniform structures such as flames or living cells is intimately involved with reaction processes. Prototype models can be cast into mathematical form, and simulated, setting up open-ended investigations for students.

SOME FUNDAMENTAL CONCEPTS. There are a few ideas that are central to systems chemistry that need to be stressed to students. I shall merely list a few of the ones that I feel are significant.

1. The macroscopic behavior of a multi-component equilibrium system, or of a multi-reaction reacting system, can be described with fewer numbers than the microscopic description of individual molecular processes.

2. A system is the superposition of individual sub-systems, but the properties of the whole are not the additive sum of the properties of the parts.

3. There is room for subjectivity and creativity in making models of chemical systems. Various models may be equally useful, and equally faithful to experimental data.

4. The best that we can sometimes accomplish is to make statements about the forms, not the details, of equations that govern a system. But sometimes it is the structure of the dynamic system, not necessarily all the details, that is significant. Thus, although probably every candle flame is different, there are common features of candle flames that arise from the structure of the mathematical model, features that yield stability and integrity to a candle flame.

SUMMARY

It has been asserted that chemistry makes its impact on the world by processes of synthesis, by putting things together. It has been predicted that this putting-together activity will increasingly involve chemists in dealing with complex systems, chemical in nature, that are of concern to a wide range of non-chemists. To deal with such research concerns in the future, as well as to make current instruction relate to issues of society as they impinge on chemistry, it seems appropriate to introduce some explicit systems chemistry into the chemistry curriculum. It is suggested that computer simulations of equilibrium systems and kinetic systems is an effective way to accomplish this, within the present structures of chemical curricula.

Case Studies in Systems Chemistry

Carboxylic Acid Equilibria

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INTRODUCTION TO CASE STUDIES IN SYSTEMS CHEMISTRY

The focus of each of these case studies is a chemical system. We shall use investigations of chemical systems to gain experience with some useful experimental techniques and theoretical methods. We shall also use these investigations to explore certain central philosophical issues, including

inter-relationships between facts and theories in science;

analytical versus synthetic approaches to learning about nature;

inter-relationships between macroscopic and microscopic descriptions;

the role of time in describing nature; and

the possibilities for subjective, creative expression in science.

The systems themselves are worth studying for their own sake. By pointing directly to significant and interesting chemical systems, we shall try to keep tangible hunks of matter -- a living cell, a lake, a beaker of solution, a jug of wine — in front of our eyes and at the front of our minds. And then, to develop realistic theories that are clearly and directly related to the real chemical systems, we shall adopt a strategy of *confrontation of data from chemical experiments with the predictions of chemical theory.* Over and over again, we shall set up confrontations by carefully designing experiments and by carefully designing chemical models so that both experiment and model yields a number that should be the same *if* experiment and model are consistent. We shall exploit the use of *computer simulation methods* for obtaining numerical predictions from our chemical models.

ACKNOWLEDGMENTS

The performance objectives for this case study were first prepared by G. M. Fleck for the General Chemistry Subcommittee of the Curriculum Committee, Division of Chemical Education, American Chemical Society, and then presented as a portion of a paper at a Symposium on Innovations in Teaching Chemistry at the 29th Two-Year College Chemistry Conference, Boston, April 1972.

Appendix I originally appeared in G. M. Fleck, Teaching Guide to Accompany Chemical Reaction Mechanisms, New York: Holt, Rinehart and Winston, Inc., 1971, pp. 82 - 91, and is reprinted by permission of Holt, Rinehart and Winston, Inc. The computer programs in this appendix are reprinted with the permission of Professor Bruce Hawkins, Department of Physics, Smith College, Northampton, Mass.

Preliminary versions of many of the FORTRAN programs have been used by the author in the instruction of introductory chemistry courses at Smith College since 1968. Some of these programs were collected together in the publication G. M. Fleck, Computer Programs for Teaching Solution Equilibria, Northampton, Mass.: 1971, © 1971 by George M. Fleck. The present forms of these programs incorporate many suggestions from students in these courses, and from undergraduate students assistants at the Smith College Computer Center.

Several of the BASIC programs were written by Trina Reed, Smith College Class of 1976, and her assistance is gratefully acknowledged.

The continuing advice and assistance of Professor Bert Mendelson, Director of the Smith College Computer Center, and Mrs. Marjorie Rolland, secretary of the Center, have been invaluable the preparation of these programs.

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Marie Chow, Smith College Class of 1974, did the programming for the Wang 700 programmable calculator, as well as assisting with many aspects of the IBM 1130 operations, and her help is greatly appreciated.

Case Studies in Systems Chemistry

CARBOXYLIC ACID EQUILIBRIA

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SOME COMMENTS ABOUT THE USE OF COMPUTERS IN THE INVESTIGATION OF SOLUTION EQUILIBRIA

Much of the material that follows is oriented toward computer calculations. There is enough computer output presented so that a student can read about the chemistry, with understanding, without having access to a computer. However, the case study is primarily intended to involve each reader with calculations and with interpretation of his or her own data, and for these purposes a computer is of great utility.

This case study attempts to present the computer as a tool that can liberate the student from dependence on the instructor and on the textbook. The case study is also viewed as a resource for the student in developing a mature understanding of the relationships among hypotheses, experimental data, and interpretation in the special field of solution equilibria. Because the computer frees both instructor and student from the limitations of paper-and-pencil calculations, it is possible to explore in detail and with assurance the consequences of various chemical assumptions about the systems being investigated.

The computer is not viewed as a substitute for laboratory experience. On the contrary, the author has found that extensive use of the computer has made possible a chemistry course in which laboratory experimentation and the use of chemical theory are very closely integrated. Throughout the case study, there is an emphasis on the confrontation of the student's own data and the quantitative predictions of the student's own model.

In the main body of the case study, use is made of FORTRAN

programming language, and the illustrative computer output has been obtained from an IBM 1130 computer system which includes an IBM 1627 strip-chart plotter. The discussion assumes that input of programs is via decks of punched cards. Our experience in chemistry instruction at Smith College has been with hands-on student use of the computer system. Some very useful plotting subroutines, available on our computer, are described in Appendix I. A single 15-minute orientation session, given to groups of about ten students at a time by an undergraduate computer-center assistant, is sufficient to provide all the information needed for running a program.

In writing this case study, as well as in teaching this material to entering college freshmen, it is assumed that the student has no previous knowledge of computers or of programming languages. Working programs are presented that can be modified easily by the changing of just a few statements. As the case study (or the semester) proceeds, the programs become somewhat more complicated, with the result that most students gain a substantial degree of facility with the computer while learning about the chemistry of equilibria in solution. Increasingly, students are entering college with some experience in FORTRAN or BASIC, and these students are encouraged to write their own programs and to attempt special computer projects.

At the end of each chapter is a section discussing the use of the BASIC programming language. The illustrative computer output has been obtained from a time-sharing terminal of the University of Massachusetts computer system. We use a Cartertone

S15C data terminal which is a modified IBM Selectric typewriter coupled to the University of Massachusetts computer center via a Bell System DATA·Phone.

All FORTRAN programs in this case study are identified by number, beginning with FORTRAN Program 1. All BASIC programs are identified by letter, beginning with BASIC Program A.

All Wang programs in this case study are identified by lower case letter, beginning with Wang Program a. We have attempted to use a Wang 700 programmable calculator with output presented on a Wang flat-bed plotter, but have found that the most convenient usage by students in studying solution equilibria is by numerical output. We have therefore given a program in this case study only for use with a Wang unit with just nixie-light output.

PERFORMANCE OBJECTIVES FOR THE CASE STUDY

GENERAL OBJECTIVES

I. You should be able to show how the predictions of a postulated set of chemical equilibria can be confronted with the quantitative facts from chemical titration experiments in such a way that the chemical model *might* be found inconsistent with the experimental data.

II. For a postulated set of chemical equilibria involving an acid with at least two dissociable protons, you should be able to show how numerical values for the equilibrium constants for that acid can be obtained from titration data of pH versus volume of added titrant.

III. For a particular acid, you should be able to obtain an experimental titration curve, analyze that data, propose a set of equilibria to serve as a chemical model, perform a computer calculation of the titration curve predicted by that model, and finally compare the results of experiment and the predictions of theory.

SPECIFIC OBJECTIVES

To achieve the three general objectives, you should be able to start with a particular set of equilibria, postulated for a particular chemical system, and deal with that chemical model and the chemical system in a stepwise fashion as outlined in the list of specific objectives that follows. Given the particular diprotic acid, you should be able to:

1. STATE A CHEMICAL MODEL. Make a list of all the chemical species that you decide should be assumed to exist in the solution. Write a balanced chemical equation for each equilibrium reaction that you decide to assume. Check to be sure that there is at least one way, via the assumed chemical reactions, for each assumed species to be produced from the chemicals that are mixed together to prepare the solution.

2. STATE THE MATHEMATICAL MODEL. Write a set of simultaneous algebraic equations as follows:

a. For each chemical reaction, write an algebraic equilibrium-constant equation in terms of molar concentrations.

b. Write the electroneutrality equation.

c. Write algebraic conservation equations in terms of molar concentrations.

3. DESIGN A TITRATION EXPERIMENT. Propose an experiment for obtaining experimental data sufficient to plot a titration curve. Decide on appropriate concentrations. Which solution will you use as titrant?

4. OBTAIN AN ALGEBRAIC PREDICTION FOR THE TITRATION CURVE. The simultaneous algebraic equations that constitute the mathematical model should be combined to give a single equation that involves (H^+), the equilibrium constants, and the known *total concentrations* (the macroscopic concentrations or analytical concentrations) of acid and base. Then change to volume variables, obtaining an equation that relates the two experimental variables (H^+) and $V_{titrant}$.

5. ESTIMATE VALUES OF THE EQUILIBRIUM CONSTANTS. Calculation of the theoretical titration curve predicted by your model requires that you have numerical values for each of the equilibrium constants. You may use a literature value for the ion product of water. Probably the most convenient assumption for the various acid dissociation constants involves use of the half-equivalence method. But however you proceed, you must put some numbers into the calculations as starting values, numbers that later can be verified or modified as calculations are compared with data.

6. PERFORM A COMPUTER SIMULATION OF THE SYSTEM. Using the algebraic equation that you obtained from the mathematical model, and using the estimated numerical values of the various equilibrium constants, use a computer to calculate a predicted titration curve. Do your data agree with the calculations? If not, then attempt to get a good fit by making appropriate changes in the

values of the equilibrium constants used in the simulation. By a series of successive approximations, you may be able to get a good fit in the regions of the titration curve where the shape of the curve is highly dependent on the values of the equilibrium constants. It may be that your data are not accurate or precise or reliable enough for this comparison; if this is the case, you must return to the laboratory and get some better data. Your results should include a set of values for the equilibrium constants, an estimate of the reliability of each constant, and a judgment of the extent to which the data are consistent with the original chemical model.

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HELPS FOR ACHIEVING THE OBJECTIVES

General objective I, the confrontation of the chemical model with experimental titration data, is achieved in specific objective 6. General objective II, evaluation of the equilibrium constants, is achieved in specific objectives 5 and 6.

Key to Textbook:

G. M. Fleck, *Equilibria in Solution*, New York: Holt, Rinehart and Winston, Inc., 1966. Objectives 1 and 2: chapter 3. Objectives 3 and 4: chapters 4 and 5.

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AN EXAMPLE OF THE CONFRONTATION OF THEORY AND EXPERIMENT:
NUMERICAL EVALUATION OF THE EQUILIBRIUM CONSTANT
FOR THE DISSOCIATION OF A MONOPROTIC ACID IN SOLUTION

During the course of the titration of an aqueous solution of a monoprotic acid with a solution of sodium hydroxide, the pH value (measured with a glass-electrode—calomel-reference-electrode assembly immersed in the solution) increases. Initially, before any sodium hydroxide titrant has been added, the pH is the pH of a solution of the pure acid in water. At the equivalence point, when equal numbers of moles of acid and base have been added to the titration vessel, the pH value is the same as the pH of a solution prepared by dissolving the sodium salt of the acid in water. Past the equivalence point, the pH continues to rise as

additional titrant is added, approaching the pH value of the sodium hydroxide solution used as titrant.

The *titration curve* is a plot of pH versus V_{NaOH}, the volume of added sodium hydroxide titrant solution. We shall examine a way to use these titration data to obtain a numerical value of the equilibrium constant for the dissociation of a *monoprotic acid*, an acid with just one dissociable proton. We shall do this by suggesting a chemical model to describe (and perhaps even partially to explain) the molecular equilibrium within the solution. Then we shall perform a computer simulation set up in such a way as to confront the model and the data. Demolition of the model is possible as a result of this confrontation. Also possible is the exposure of bad data. In this discussion, we shall follow an organization suggested by the *acid-base equilibria* specific objectives 1 - 6 for a diprotic acid.

Let us consider the titration of 0.1000 molar acetic acid solution with 0.1000 molar sodium hydroxide solution at room temperature.

OBJECTIVE 1. STATE A CHEMICAL MODEL.

List of chemical species assumed:

HA acetic acid

A^- acetate ion

Na^+

OH^-

H^+

H_2O

Equilibria assumed:

$$HA \rightleftarrows A^- + H^+$$

$$H_2O \rightleftarrows OH^- + H^+$$

OBJECTIVE 2. STATE THE MATHEMATICAL MODEL.

a. Equilibrium Constant Equations:

$$K = \frac{(A^-)(H^+)}{(HA)} \qquad \text{(i)}$$

$$K_w = (OH^-)(H^+) \qquad \text{(ii)}$$

where (A^-), (HA), (H^+), and (OH^-) are individual-species concentrations (microscopic concentrations) in moles/liter.

b. Electroneutrality Equation:

$$(Na^+) + (H^+) = (OH^-) + (A^-) \qquad \text{(iii)}$$

c. Conservation Equations:

$$[A] = (HA) + (A^-) \qquad \text{(iv)}$$

$$[Na] = (Na^+) \qquad \text{(v)}$$

where [A] and [Na] are total concentrations of all acetate-containing species and of all sodium-containing species.

OBJECTIVE 3. DESIGN A TITRATION EXPERIMENT. The goal of this experiment is to obtain a set of ordered pairs $\{(H^+), V_{NaOH}\}$ for representative points in the titration, all the way from the start to past the equivalence point. Note that the experimental variables, as directly observed in the laboratory, are pH and V_{NaOH}.

OBJECTIVE 4. OBTAIN AN ALGEBRAIC EQUATION FOR THE TITRATION CURVE. Equations i through v, a set of five simultaneous equations in five unknowns, constitute the mathematical model for this acid-base titration. We seek to eliminate four of these unknowns and thereby obtain a single equation relating known quantities in [ ]'s to the measurable (H^+). Equations i and iv can be combined to eliminate (HA), giving

$$[A] = \left(\frac{(H^+)}{K} + 1\right)(A^-) \qquad \text{(vi)}$$

Equations iii and v together yield

$$(A^-) = (H^+) - (OH^-) + [Na] \qquad \text{(vii)}$$

We now put everything together. Equations vi, vii, and also ii, are combined, resulting in the following cubic equation in (H^+):

$$(H^+)^3 + \{[Na] + K\}(H^+)^2 + \{K[Na] - K[A] - K_w\}(H^+) - K_wK = 0 \qquad \text{(viii)}$$

Our titration is performed by mixing two solutions: a

solution of acid having concentration [A] = M_A and volume V_A; and a solution of base having concentration [Na] = M_{Na} and volume added at any particular point in the titration equal to V_{Na}. If there is additivity of volumes upon mixing (that is, if $V_{solution}$ is equal to the sum $V_A + V_{Na}$), then we can write the two macroscopic (total) concentrations for the solution being titrated as

$$[A] = \frac{V_A M_A}{V_A + V_{Na}} \quad \text{and} \quad [Na] = \frac{V_{Na} M_{Na}}{V_A + V_{Na}} \qquad \text{(ix and x)}$$

During the course of the titration, only (H^+) and V_{Na} are variables. We shall now substitute Equations ix and x into Equation viii to give

$$V_{Na} = -V_A \cdot F \qquad \text{(xi)}$$

where the fraction F is the following ratio of two polynomials in (H^+):

$$F = \frac{(H^+)^3 + K(H^+)^2 - \{K_w + K \cdot M_A\}(H^+) - K_w K}{(H^+)^3 + \{K + M_{Na}\}(H^+)^2 + \{K \cdot M_{Na} - K_w\}(H^+) - K_w K}$$

OBJECTIVE 5. ESTIMATE A VALUE FOR THE EQUILIBRIUM CONSTANT. Try the half-equivalence method for getting a trial value of the equilibrium constant K to include in the calculations that depend on Equation xi. The half-equivalence method asserts that $(H^+) = K$ (and therefore that pH = pK) at the point in the titration at which V_{Na} has a value equal to just *half* its value at the equivalence point. Thus, half-way between the beginning of the titration and the equivalence point, the pH has a value that permits a good guess for the value of K.

OBJECTIVE 6. PERFORM A COMPUTER SIMULATION OF THE TITRATION CURVE. Now use Equation xi to calculate a titration curve, the curve predicted *for your own experimental conditions, for your acid, for your estimated value for* K, expressed as a plot of pH versus V_{Na}. The procedure is to assume a value for (H^+) and then to use Equation xi to calculate the corresponding value of V_{Na}. If this volume is negative, the calculation is rejected as not corresponding to a point in the domain of chemical reality, and

another value of (H^+) is picked. This process is repeated over and over, and the positive values of volumes are recorded.

These repetitive calculations can readily be performed by a digital computer or a programmable calculator. A FORTRAN program that will accomplish our task is given below:

```
// JOB
// FOR
* LIST SOURCE PROGRAM
*IOCS(CARD, 1132 PRINTER)
C      TITRATION CURVE       ACETIC ACID
       REAL K, KW, NUM, MA, MNA
       VA = 25.00
       MA = 0.1000
       MNA = 0.1000
       K = 1.75E-5
       KW = 1.008E-14
       PH = 0.00
     1 PH = PH + 0.10
       H = 10**(-PH)
       NUM = H**3 + K*(H**2) - (KW+(K*MA))*H-KW*K
       DEN = H**3 + (K+MNA)*(H**2) + (K*MNA-KW)*H - KW*K
       VNA = -VA*NUM/DEN
       IF (VNA) 2, 20, 20
     2 IF (PH - 7.00) 1, 1, 30
    20 WRITE (3,10) VNA, PH
    10 FORMAT (F10.3, F10.3)
       GO TO 1
    30 CALL EXIT
       END
// XEQ
```

Code for Translating Program into Algebra

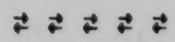
FORTRAN Symbol	Algebraic Symbol
K	K
KW	K_w
VA	V_A
VNA	V_{Na}
MA	M_A
MNA	M_{Na}
PH	pH
H	(H^+)
*	×
**	raised to the power of

The output of this program is a long tabulation of ordered pairs of numbers, where the first number is the volume of titrant added and the second number is the resulting pH value. As a sample, the first few pairs in the tabulation are given below:

volume of titrant →		← pH
	0.027	2.899
	0.178	2.999
	0.337	3.099
	0.513	3.199
	0.714	3.299
	0.949	3.399

Of course, there are many other ways to display the results of the calculations, and you may have your own ideas about the best way to set up your confrontation of model and data.

Compare calculated numbers with numbers from your own lab data book. If they don't match, try the calculations again with a different value of K. Maybe you should also change K_w. Can you match your data and the calculated curve by choice of K? If so, what is the best value of K? How reliable do think the value of your best K is? Express K as some number, ± some error estimate. If you can't match data and calculations, then report what, in your judgment, is the problem. If you suspect the data, then return to the laboratory and get additional data which are more reliable.



Chapter 1

Titration of a Monoprotic Acid

CARBOXYLIC ACIDS: A COMMON CLASS OF COMPOUNDS

Some would say that the simplest of the carboxylic acids is CARBONIC ACID, a chemical compound that has never been prepared as a pure substance. Carbonic acid (H_2CO_3) appears to exist only in solution. A solution that contains carbonic acid can be prepared by bubbling carbon dioxide gas (CO_2) through water. This formation of carbonic acid can be described by the chemical equation

$$CO_2 + H_2O \rightleftarrows H_2CO_3 \qquad (1)$$

Equation 1 is a symbolic chemical model, written to describe some observations.

Does carbonic acid really exist? Is it a real compound? Perhaps. But real or not, H_2CO_3 is a useful chemical species to use in describing some very real reactions of carbonates, bicarbonates, and carbon dioxide with acids, bases, and water. A common model of these reactions consists of the reactions of carbonic acid, bicarbonate ion, and carbonate ion, written as the pair of chemical equations

$$H_2CO_3 \rightleftarrows H^+ + \underset{\text{bicarbonate}}{HCO_3^-} \qquad (2)$$

$$HCO_3^- \rightleftarrows H^+ + \underset{\text{carbonate}}{CO_3^{--}} \qquad (3)$$

In many respects, Equations 2 and 3 have been found to describe faithfully the observed behavior of solutions. This chemical model has been found to be consistent with experimental observation.

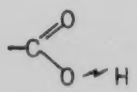
Carbonic acid has only a few atoms per molecule, and it may appear to be a simple species. However, description of a system containing carbonic acid may require Equations 1, 2, and 3, as well as

the equation for the dissociation of the solvent,

$$H_2O \rightleftharpoons H^+ + OH^-$$

A solution containing carbonic acid can be described as a system of coupled and competing simultaneous chemical reactions. Such a solution may be a rather complicated chemical system. We shall find that many aspects of carboxylic acid equilibria can be discovered in a study of a monoprotic acid (an acid that has only one proton that dissociates) such as formic acid, acetic acid, or one of the other acids whose structures are given in Table 1. We shall think about the system at equilibrium, ignoring the rate and the manner by which the system achieves its equilibrium state. Then we shall look at additional features of carboxylic acid systems by examining some diprotic acids in which each proton dissociates from a separate site (proton binding sites are not unambiguously definable for the various carbonic acid species). We shall return at last to carbonic acid, but this return will be in the form of a literature-search and literature-interpretation project.

A molecule of a carboxylic acid listed in Table 1 contains the structural unit



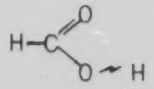
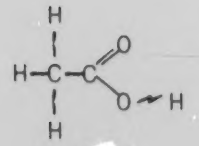
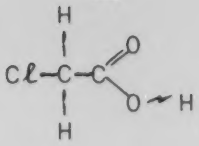
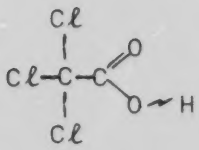
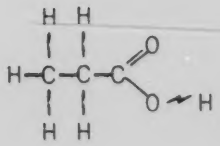
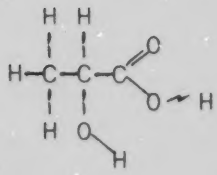
called the CARBOXYL GROUP. The proton can dissociate, giving the carboxylate anion and the hydrogen ion:

and H^+

We shall now focus on compounds that contain just one of these carboxyl groups.

Table 1

STRUCTURES OF SOME MONOPROTIC CARBOXYLIC ACIDS

	formic acid
	acetic acid
	monochloroacetic acid
	trichloroacetic acid
	propionic acid
	lactic acid

CHEMICAL MODEL FOR A MONOPROTIC CARBOXYLIC ACID

Let us imagine a monoprotic acid that can exist in solution both as the associated acid HA and as the dissociated anion A^-. Such a situation can exist with any of the compounds given in Table 1. Solutions can be prepared by mixing quantities of the acid, the sodium salt, sodium hydroxide, and water. Such solutions may have pH values that range from the acidic region to the basic region. We shall construct a model for this system that allows the prediction of pH values from statements of the amounts of acid, base, and solvent used for preparing the solution. In order to make this discussion specific, we shall focus on the titration of a carboxylic acid with sodium hydroxide.

The species present in solution are (we shall assume) as follows:

$$H_2O,\ HA,\ A^-,\ Na^+,\ H^+,\ OH^- \qquad (4)$$

The chemical equilibria required to establish equilibrium in this system are (we shall asume) as follows:

$$H_2O \rightleftarrows H^+ + OH^- \qquad (5)$$

$$HA \rightleftarrows H^+ + A^- \qquad (6)$$

This listing of the chemical species assumed, together with this listing of the chemical equilibria assumed, constitutes the *chemical model for the system.*

Associated with each chemical reaction is an *equilibrium-constant equation* which we shall always write in a standard form, with the molar concentration of a chemical species symbolized by enclosing the formula of the species with ( ), and with the equilibrium constant symbolized by a capital letter K with some identifying subscript. Thus we write, to accompany Reactions 5 and 6, the algebraic equations

$$K_w = (H^+)(OH^-) \qquad (7)$$

$$K_{HA} = \frac{(H^+)(A^-)}{(HA)} \qquad (8)$$

The numerator in each equation is a product of concentrations of *reaction products*, and the denominator in each case is a product of concentrations of *reactants*, with the terms "product" and "reactant" defined in terms of the chemical reaction equation as it is written in the chemical model. When the solvent occurs in a chemical reaction, its concentration does not appear in the equilibrium-constant equation; instead, we write the number one in its place. These equilibrium constants may be expected to have constant numerical values under constant conditions, but they will in general be functions of temperature, pressure, solvent, and concentration. Hopefully, an equilibrium constant will not change its value very much with concentration within the concentration range which is encountered in the experiments under consideration.

The requirement of electrical neutrality of the solution requires that the number of positive charges in the solution be equal to the number of negative charges in solution. Written in terms of molar concentrations, the *electrical neutrality equation* is

$$(A^-) + (OH^-) = (H^+) + (Na^+) \qquad (9)$$

We shall also require that there be conservation of mass and non-transmutation of elements, and that chemical reactions that are not included in the model do not occur. Such requirements can be stated algebraically in terms of a set of *conservation equations*, of which we shall require two here:

$$[A] = (HA) + (A^-) \qquad (10)$$

$$[Na] = (Na^+) \qquad (11)$$

Equation 10 states that all the carboxylic acid originally placed in solution is distributed between the species HA and A^-. The quantity [A] represents the total of all A-containing species, in moles per liter. Equation 10 is an algebraic statement that the acid, when added to water, cannot disappear, but can be transformed into any of the species of the model if there is a chemical equation for the transformation. Since there is only one sodium-containing species in the model, Equation 11 is particularly simple.

It is helpful to distinguish between two sorts of concentrations: we shall speak of *macroscopic concentrations*, symbolized by letters enclosed by [ ]'s, and *microscopic concentrations*, symbolized by letters enclosed by ( )'s. Macroscopic concentrations can generally be known by the experimenter from the manner in which the solutions were prepared; macroscopic concentrations are thus experimentally observable quantities. Microscopic concentrations are concentrations of individual chemical species, and often these concentrations can be found only by interpreting experimental data in terms of a model. One goal of our manipulations of this model of an acid is to obtain ways to relate observable macroscopic concentrations and the microscopic concentrations of the species listed in the chemical model.

MATHEMATICAL MODEL FOR A MONOPROTIC CARBOXYLIC ACID

Equations 7, 8, 9, 10, and 11 comprise a set of simultaneous algebraic equations that describe in quantative terms the chemical model of a carboxylic acid. This set of equations is the *mathematical model for the system*. These five equations can be combined to

eliminate all the microscopic concentrations except (H^+), giving the cubic equation

$$(H^+)^3 + \{[M] + K_{HA}\}(H^+)^2 + \{K_{HA}[M] - K_{HA}[A] - K_w\}(H^+) - K_wK_{HA} = 0 \quad (12)$$

This equation is written in terms of a rather special microscopic concentration, (H^+), which is used here as a *master variable*. We shall use (H^+) to describe the chemistry of the system, largely because of the relationship between (H^+) and the experimentally measurable quantity, pH. We shall assume the equation

$$pH = -\log_{10}(H^+) \quad (13)$$

where pH is the reading on a properly-standardized pH meter, and (H^+) is the molar concentration of the species called the hydrated hydrogen ion, or the hydronium ion.

It appears, from a casual inspection of Equation 12, that there are two macroscopic variables: [A] and [M]. In an ordinary titration, however, [A] and [M] are not independent variables. It all becomes clearer if we change variables so as to make the actual experimental variable—the volume of sodium hydroxide titrant added to the acid solution, called V_{NaOH}—explicit and prominent in the equation. If the two solutions used in a titration contain only the solutes HA and NaOH respectively, if we call the volumes of the two solutions that have been mixed V_{HA} and V_{NaOH}, and if the volumes of the two solutions are additive (that is, if $V_{total} = V_{HA} + V_{NaOH}$), then

$$[A] = \frac{V_{HA}M_{HA}}{V_{HA} + V_{NaOH}} \quad (14)$$

and

$$[M] = \frac{V_{NaOH} M_{NaOH}}{V_{HA} + V_{NaOH}} \qquad (15)$$

where V_{NaOH} is the volume of sodium hydroxide titrant added,

V_{HA} is the original volume of carboxylic acid solution,

M_{NaOH} is the molarity of the sodium hydroxide solution, and

M_{HA} is the molarity of the carboxylic acid solution.

Introduction of Equations 13 and 14 into Equation 12 permits the elimination of [A] and [M], and gives an equation that relates the two experimental variables (H^+) and V_{NaOH}. The equation is

$$V_{NaOH} = -V_{HA}\left(\frac{numerator}{denominator}\right) \qquad (16)$$

$$numerator = (H^+)^3 + K_{HA}(H^+)^2 - \{K_w + K_{HA}M_{HA}\}(H^+) - K_wK_{HA}$$

$$denominator = (H^+)^3 + \{K_{HA} + M_{NaOH}\}(H^+)^2 + \{K_{HA}M_{NaOH} - K_w\}(H^+) - K_wK_{HA}$$

EXERCISES

1. Combine the appropriate algebraic equations and obtain Equation 12.

2. Learn about the use and limitations of Equation 13. One authoritative source of information is R. G. Bates, *Determination of pH*, New York: John Wiley & Sons, Inc., 1964.

3. Perform the algebra that takes you from Equations 12, 14, and 15 to Equation 16.

PREDICTIONS OF THE MODEL FOR A TITRATION EXPERIMENT

In a titration experiment, quantities of the titrant are dispensed from a burette into a solution of acid, with the volume of added titrant being recorded after each addition. The pH of the resulting solution is measured, after each addition of titrant. There results a pair of two numbers, V_{NaOH} and pH, which characterizes the solution at each point in the titration. More titrant is added, and a new set of numbers, V_{NaOH} and pH, are recorded. When this process is continued throughout the titration, a set of ordered pairs $\{V_{NaOH}, pH\}$ is obtained that can be plotted as a *titration curve of the carboxylic acid*. If required, we can use the operational definition

$$pH = -\log_{10}(H^+)$$

to convert the ordered pairs $\{V_{NaOH}, pH\}$ into the ordered pairs $\{V_{NaOH}, (H^+)\}$. Our task, in using our model to simulate this titration experiment, is to obtain a predicted titration curve in a form suitable for comparing with actual experimental data.

Numerical substitution of a value of (H^+) into Equation 16 yields a value of V_{NaOH}, provided that numerical values for K_{HA} and K_w are already known, or are assumed.

> Methods for making reasonable estimates of the numerical values of these two equilibrium constants will be discussed in a later section. For purposes of understanding the following computer programs, just assume that the appropriate numbers have somehow been revealed. If you have your own data, and want to make a prediction of the titration curve, you should jump ahead to the later section, and find out how to make an informed guess.

We shall program the IBM 1130 computer to perform this calculation for us for many values of (H^+). A program that will accomplish

this task is FORTRAN Program 1, listed on page 28, with sample output given on pages 28 and 29. Let us examine this program, since it is typical of programs that can do the drudgery of repetitive calculations for us, leaving us free to think about interpretations and meaning of the numbers.

Each typewritten line in this program is called a *statement*. In each case, the statement was given to the computer in the form of a single punched card. The first four cards are *control cards;* they must be present and in the proper order for the program to function. (Actually, the * LIST SOURCE PROGRAM statement is not needed for the program to function; when it is included, the printer will type out the program as it appears on page 28. Such a printout is helpful in spotting mistakes when you are running the program for the first time; later on, you may find that such a listing of the program takes too much time, and is not helpful, and you will then want to remove this control card.) The C on each of the next three cards indicates a *comment card*. A comment card does not carry instructions to the computer for the program, but is included only to remind the user of special features of the program.

A special feature of the FORTRAN language that is often helpful, but is annoying to us at this point, is the use of the letters I, J, K, L, M, and N (the letters from I to N, the first two letters of INteger) as first letters of variables used as integers. Integers are numbers without decimal points. Since we shall wish to use the variable names KHA, KW, NUM, MHA, and MMOH (because they remind us of K_{HA}, K_w, numerator, M_{HA}, and M_{NaOH}), we tell the computer that we intend to violate these rules of FORTRAN grammar; we include the statement REAL KHA, KW, NUM, MHA, MMOH. In FORTRAN, the word "real" is used to describe numbers with decimal points.

A series of cards follows next to define various variables and

1

```
// JOB                  S71007,S51


// FOR
* LIST SOURCE PROGRAM
*IOCS(CARD, 1132 PRINTER)

C       TITRATION CURVE
C       PREDICTIONS OF THE CHEMICAL MODEL
C       MONOPROTIC ACID, ASSUMED VALUE OF KHA

        REAL KHA, KW, NUM, MHA, MMOH
        KHA = 1.75E-5
        VHA = 25.00
        MHA = 0.1000
        MMOH = 0.1000
        KW = 1.008E-14

        H = 1.
      1 H = .5*H
        PH = -(ALOG(H))/2.303
        NUM = H**3 + KHA*(H**2) - (KW + (KHA*MHA))*H - KW*KHA
        DEN =  H**3 + (KHA + MMOH)*(H**2) + (KHA*MMOH - KW)*H - KW*KHA
        VMOH = -VHA*NUM/DEN
        IF (VMOH) 2, 20, 20
      2 IF (PH - 7.00) 1, 1, 30
     20 WRITE (3,10) VMOH, PH
     10 FORMAT (F10.3, F10.3)
        GO TO 1
     30 CALL EXIT
        END

// XEQ
```

PRINTER OUTPUT:

```
     0.194      3.009
     0.739      3.310
     1.607      3.611
     3.100      3.912
     5.552      4.213
     9.100      4.514
    13.349      4.815
    17.406      5.116
    20.524      5.417
    22.542      5.718
    23.707      6.019
    24.336      6.320
    24.663      6.621
```

24.830	6.922
24.915	7.223
24.957	7.524
24.979	7.825
24.990	8.126
24.996	8.427
25.000	8.728
25.004	9.029
25.010	9.330
25.021	9.631
25.043	9.932
25.086	10.233
25.173	10.534
25.348	10.835
25.702	11.136
26.424	11.437
27.933	11.738
31.232	12.039
39.239	12.340
64.818	12.640
416.096	12.941

constants, and to state the initial conditions of the titration. Since only capital letters (and no subscripts) are available for communicating with the computer, we use such expressions as KHA and VHA to represent K_{HA} and V_{HA}. The writer of this program thought that M_{NaOH} could be most clearly represented by MMOH rather than by MNAOH; you can use whatever combination of letters you wish, with a maximum of five letters per variable name. Large and small numbers are written in *exponential notation*, which means that two of the FORTRAN statements translate as follows:

KHA = 1.75E-5 ⇒ $K_{HA} = 1.75 \times 10^{-5}$

KW = 1.008E-14 ⇒ $K_{w} = 1.008 \times 10^{-14}$

Most of the remaining cards contain statements that constitute a *computation loop*, and we shall look at this loop in detail later. Statement 30 and the following card provide the necessary mechanism for ending the program. The last card in the deck is the instruction to execute the program.

Unless there are instructions to the contrary, the computer proceeds sequentially through the statements. After one statement has been executed, the statement immediately following it is then executed. However, you as the programmer may change the sequence of operations by using the GO TO or IF statements:

¶The statement

```
GO TO 1
```

will be followed by execution of the statement numbered 1. Then the program follows sequentially after statement 1.

¶The statement

```
IF (A) 1, 2, 3
```

30

provides for transfer of the program to one of three different statements, depending on the numerical value of the variable A. If A is negative, then the next statement executed will be the statement numbered 1. If A is zero, then the next statement that is executed will be statement 2. If A is positive, then the next statement executed will be statement 3.

Note that only some of the statements are numbered. You may number any statement with any number, remembering to never use the same number twice.

You can add spaces within a statement, almost at your own convenience, in order to make the typewritten statement more readable to you. If there is doubt in your mind about the order in which the computer will perform the indicated arithmetic within a statement, then add some clarifying parentheses; parentheses have the same meaning in FORTRAN as in arithmetic and algebra. You must always use a closing parenthesis with each opening parenthesis. Other arithmetic symbols used are:

\+ *addition sign*

\- *subtraction sign*

/ *division sign*

* *multiplication sign* (do not indicate multiplication with just parentheses)

** means *raised to the power of*

= *equals sign*

The printer instructions to print ordered pairs of values of VMOH and PH can be written as

```
    WRITE (3,10) VMOH  PH
10 FORMAT (F10.3, F10.3)
```

where the 3 in the WRITE statement is the code number for the printer,

and the 10 refers to FORMAT statement 10, which gives some details about how the printer is to print the output. The list of variable names in the WRITE statement indicates the variables whose numerical values will be printed by the printer. The notation 10.3 means that a total of ten spaces has been reserved for typing the number, with three places following the decimal point. The F (*for "floating point"*) means that the number will be printed as an ordinary number with a decimal point (that is, not in exponential notation, and not as an integer).

The heart of this particular FORTRAN program is the computation loop. A large value (larger than will be encountered in the actual titration) for (H^+) is assumed; the concentration of H^+ is symbolized by the letter H. Then this value for (H^+) is reduced to 50% of its previous value in statement 1, the pH value is calculated for future reference, and then (H^+) is substituted into Equation 16. A value of titrant volume is calculated, and it is tested in two IF statements to see if it is negative, positive, or zero; and if it is negative, whether the titration is in the acidic or basic region. Only positive values of volume are acceptable as having any chemical meaning. Negative values are encountered at the beginning of the calculations, and here the computation loop cycles without any output being printed. When (H^+) gets small enough to produce a positive volume, the cycle begins to include the WRITE statement and output results. Finally, when (H^+) becomes smaller than its value in the titrant itself, the calculations pass outside the realm of chemical reality, the volume becomes negative, and the program is terminated.

2

```
// JOB                    S71007,S51


// FOR
* LIST SOURCE PROGRAM
*IOCS(CARD, 1132 PRINTER)

C      TITRATION CURVE
C      PREDICTIONS OF THE CHEMICAL MODEL
C      MONOPROTIC ACID, ASSUMED VALUE OF KHA

       REAL KHA, KW, NUM, MHA, MMOH
       KHA = 1.75E-5
       VHA = 25.00
       MHA = 0.1000
       MMOH = 0.1000
       KW = 1.008E-14

       H = 1.
     1 H = .8*H
       PH = -(ALOG(H))/2.303
       NUM = H**3 + KHA*(H**2) - (KW + (KHA*MHA))*H - KW*KHA
       DEN =  H**3 + (KHA + MMOH)*(H**2) + (KHA*MMOH - KW)*H - KW*KHA
       VMOH = -VHA*NUM/DEN
       IF (VMOH) 2, 20, 20
     2 IF (PH - 7.00) 1, 1, 30
    20 WRITE (3,10) VMOH, PH
    10 FORMAT (F10.3, F10.3)
       GO TO 1
    30 CALL EXIT
       END

// XEQ
```

PRINTER OUTPUT:

```
     0.038      2.906
     0.184      3.003
     0.339      3.100
     0.510      3.197
     0.703      3.294
     0.928      3.391
     1.194      3.488
     1.509      3.585
     1.886      3.681
     2.336      3.778
     2.871      3.875
     3.502      3.972
     4.240      4.069
```

5.093	4.166
6.064	4.263
7.151	4.360
8.346	4.457
9.632	4.553
10.984	4.650
12.372	4.747
13.764	4.844
15.124	4.941
16.422	5.038
17.632	5.135
18.737	5.232
19.725	5.329
20.594	5.425
21.347	5.522
21.989	5.619
22.532	5.716
22.986	5.813
23.362	5.910
23.672	6.007
23.926	6.104
24.134	6.201
24.302	6.298
24.438	6.394
24.549	6.491
24.637	6.588
24.709	6.685
24.767	6.782
24.813	6.879
24.850	6.976
24.880	7.073
24.904	7.170
24.923	7.266
24.938	7.363
24.950	7.460
24.960	7.557
24.968	7.654
24.975	7.751
24.980	7.848
24.984	7.945
24.987	8.042
24.990	8.138
24.992	8.235
24.994	8.332
24.996	8.429
24.997	8.526
24.998	8.623
24.999	8.720
25.001	8.817
25.002	8.914
25.003	9.011
25.005	9.107
25.007	9.204
25.009	9.301
25.012	9.398
25.015	9.495
25.019	9.592
25.024	9.689
25.030	9.786
25.038	9.883
25.048	9.979
25.060	10.076
25.075	10.173
25.094	10.270
25.118	10.367
25.147	10.464
25.184	10.561
25.231	10.658
25.289	10.755
25.362	10.851
25.454	10.948
25.568	11.045
25.713	11.142
25.894	11.239
26.123	11.336
26.412	11.433
26.777	11.530
27.242	11.627
27.834	11.724
28.594	11.820
29.575	11.917
30.852	12.014
32.536	12.111
34.789	12.208
37.866	12.305
42.188	12.402
48.506	12.499
58.296	12.596
74.933	12.692
108.185	12.789
203.028	12.886
2050.702	12.983

Perhaps you may feel that the output listed on pages 28 and 29 inadequate to give a realistic prediction of a titration curve that is, in fact, a continuous function. Some of the output pairs are rather widely spaced. It is easy to get the output more-closely spaced; we simply make the decrements in (H^+) smaller in Statement 1. Such a revised program, together with the resultant output, is given as FORTRAN Program 2 on pages 33 and 34.

A GRAPHICAL PREDICTION OF THE MODEL FOR A TITRATION EXPERIMENT

The numerical output of the previous computer calculations is a prediction with greater precision than the corresponding experimental data. However, most people find it rather difficult to visualize the shape of the predicted function by looking at the long listing of ordered pairs of numbers. The computer program which we shall now examine yields a graphical prediction. The principal readout from the computer is a graph of the titration curve, drawn and labelled by the plotter. The program, FORTRAN Program 3, is presented on page 37 and the plotter output is given on page 38. We shall examine some aspects of this program which pertain to the use of the plotter as the output device.

PLOTTER PREPARATION SUBROUTINE

The plotter preparation statement in the program is of the form

```
CALL PREP (XS, YS, XO, YO)
```

where

XS is the scale chosen for the x-axis, written in inches per unit, using a number with a decimal point.

YS is the scale chosen for the y-axis, written in inches per unit, using a number with a decimal point.

XO is the distance in inches from the left-hand edge of the graph to the origin. Include decimal point.

YO is the distance in inches from the bottom of the graph to the origin. Include decimal point.

WRITE STATEMENT

The statement in the program

```
WRITE (7,15) KHA
```

tells the computer to write, using the plotter (the plotter has the code number 7), the numerical value of K_{HA} according to the format given in statement 15. The format information contained in statement 15 tells the computer to write the characters typed on the card between the two ' marks. This statement is used to provide a label for the graph. Similar statements are used to label the x-axis and the y-axis.

Following the CALL PREP statement, a WRITE (7,) statement results in a label placed at the top of the graph. Following each of the CALL XAXIS and CALL YAXIS statements, a WRITE (7,) statement results in a label placed along the corresponding axis. Other words and characters can be placed anywhere on the graph; see the IBM plotter instruction manual for detailed instructions.

SUBROUTINE YAXIS

SUBROUTINE XAXIS

The y-axis statement in the program is of the form

```
CALL YAXIS (X,Y,U,N,NLAB)
```

where

X and Y are the coordinates of the origin of the axes.

U is the distance between tick marks on the y-axis.

N is the number of tick marks; thus N × U is the length of the y-axis.

NLAB is the number of tick marks that are to be labelled with the value of the scale at that point.

The corresponding statement is used for the x-axis.

3

```
// JOB                    S71007,S51


// FOR
*ONE WORD INTEGERS
* LIST SOURCE PROGRAM
*IOCS(CARD, 1132 PRINTER, TYPEWRITER, PLOTTER)
C       TITRATION CURVE

C       PREDICTIONS OF THE CHEMICAL MODEL

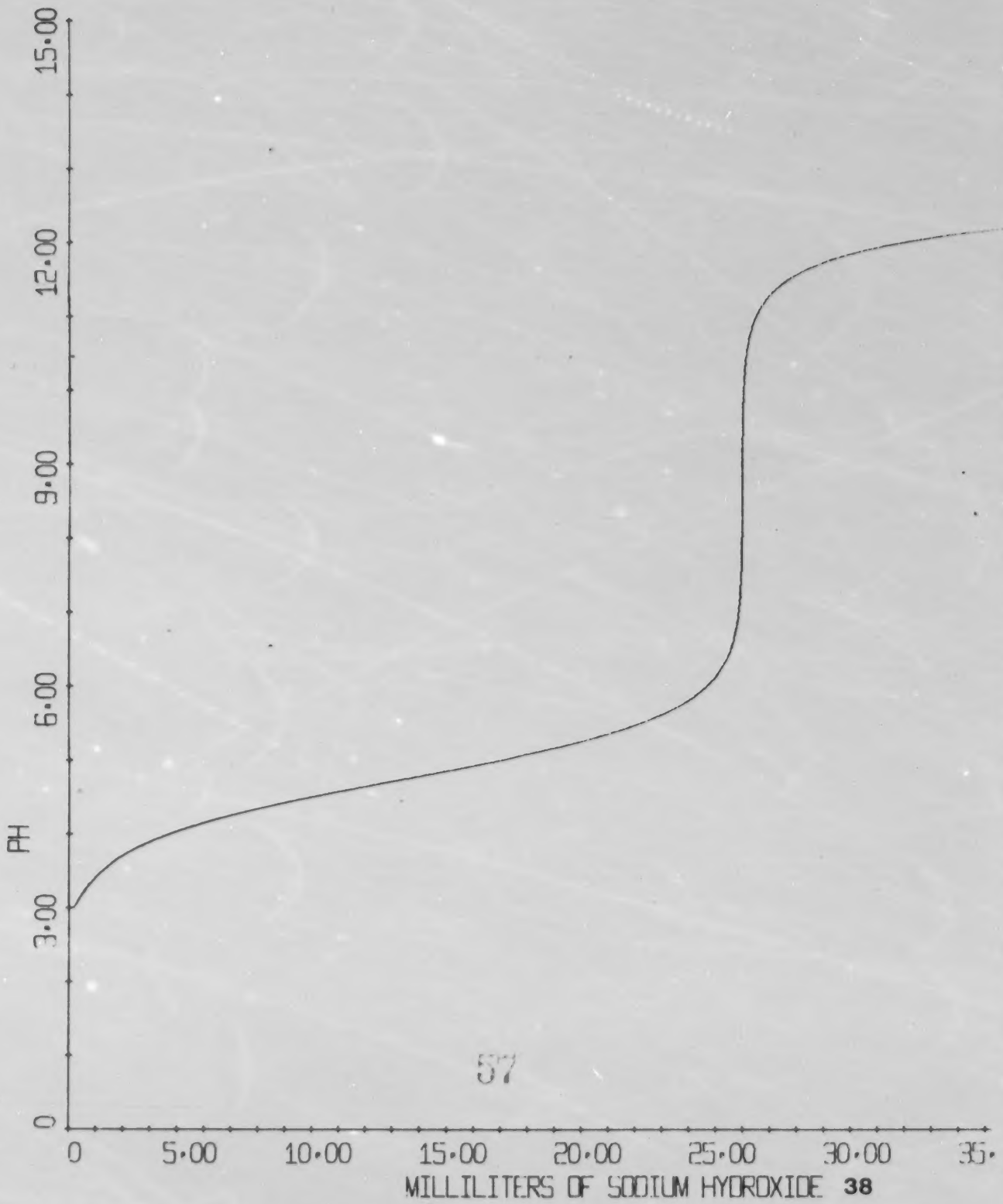
C       MONOPROTIC ACID, ASSUMED VALUE OF KHA

        REAL KHA, KW, NUM, MHA, MMOH
        KHA = 1.75E-5
        VHA = 25.00
        MHA = 0.1000
        MMOH = 0.1000
        KW = 1.008E-14
        CALL PREP (.2, .55, 1., 1.)
        WRITE (7,15) KHA
   15 FORMAT ('PREDICTION OF A CHEMICAL MODEL WITH KHA =',E11.3)

C       CALCULATION AND PLOTTING OF THE TITRATION CURVE
        H = 1.
    1   H = .5*H
        PH = -(ALOG(H))/2.303
        NUM = H**3 + KHA*(H**2) - (KW + (KHA*MHA))*H - KW*KHA
        DEN =  H**3 + (KHA + MMOH)*(H**2) + (KHA*MMOH - KW)*H - KW*KHA
        VMOH = -VHA*NUM/DEN
        IF (VMOH) 1,2,2
    2   CALL FPLOT (-2,VMOH,PH)
    5   H = H - .1*H
        PH = -(ALOG(H))/2.303
        DEN =  H**3 + (KHA + MMOH)*(H**2) + (KHA*MMOH - KW)*H - KW*KHA
        NUM = H**3 + KHA*(H**2) - (KW + (KHA*MHA))*H - KW*KHA
        VMOH = -VHA*NUM/DEN
        IF(50.-VMOH) 10,3,3
    3   CALL FPLOT (0,VMOH,PH)
        GO TO 5

C       DRAWING AND LABELLING THE AXES
   10   CALL YAXIS (0., 0., 1., 15, 5)
        WRITE (7,17)
   17   FORMAT ('PH')
        CALL XAXIS (0.,0.,1.,50,10)
        WRITE (7,16)
   16   FORMAT ('MILLILITERS OF SODIUM HYDROXIDE')
        CALL FINPL
        CALL EXIT
        END


// XEQ
```


PREDICTION OF A CHEMICAL MODEL WITH KHA = 0.175E-04
PH
0
3.00
6.00
9.00
12.00
15.00
0
5.00
10.00
15.00
20.00
25.00
30.00
35.
MILLILITERS OF SODIUM HYDROXIDE

EVALUATION OF EQUILIBRIUM CONSTANTS BY COMPARING PREDICTIONS OF A MODEL WITH THE DATA FROM A TITRATION EXPERIMENT

If we proceed to interpret experimental data according to the chemical model described on page 21 we shall have reduced all the differences between various monoprotic acids simply to the differences in the values of the equilibrium constant K_{HA}. Since we intend to describe the particular acid by specifying the numerical value of its equilibrium constant, it is important that we have a reliable method for evaluating that equilibrium constant.

The shape of the titration curve depends on the value of the equilibrium constants K_{HA} and K_w. Thus it would seem that one way of obtaining a good value for the equilibrium constants would be to find the values for K_{HA} and K_w that yield a titration curve that gives the best fit to experimental data from an actual titration experiment. This is, in fact, what we shall do.

FORTRAN Programs 1, 2, and 3 each give predictions of the titration curve for a monoprotic acid. In each case, however, it is necessary to supply a numerical value for both of the equilibrium constants before any calculations can be made. Thus we need a way to make an informed guess for such numbers. Then we need a convenient way to plot the predictions of the model on the same graph as the experimental data; or a convenient way to list the predictions of the model in the same table as the experimental data. We shall proceed first to develop two ways—one numerical and one graphical—to use the computer to facilitate a comparison of data and model for various values of the equilibrium constants.

FORTRAN Program 4 has been written to accept (as input) your experimental data from a titration, and to yield output as a tabular comparison of observed and calculated values of titrant volume for each of the experimental pH values. The input data are in the form of a set of ordered pairs $\{V_{NaOH}, pH\}$. Each pair of numbers is punched on a separate card, and the computer reads these cards one by one. From each card, the card-reader reads the values of V_{NaOH} and pH. The computer converts each pH value to a value of (H^+), and calculates a value of V_{NaOH} which we shall call VMOH (CAL). Then the computer prints out VMOH (CAL) and the experimental value of V_{NaOH} called VMOH (EXP) originally read from the card.

Statements 28 and 25 give instructions to the card reader (the number 2 is the code number for the card reader) to read the next card in the hopper, to interpret any number punched in the first 20 spaces as V, and to interpret any number in the next 20 spaces as PH. The computer (because of FORMAT statement 25) expects that each number will have a decimal point; no matter how many decimal places are in the punched number, the number will be read with two decimal places and additional digits will be ignored. These data cards are placed immediately following the // XEQ card.

Every program requires a mechanism for ending itself. Here we use the device of placing a negative number in the first 20 spaces. The IF statement following statement 25 transfers the program to tne next statement for each data card that actually contains experimental data (all experimental volumes are zero or positive), but terminates the program when V is negative. Thus, by punching the last data card with a negative value of volume, we end the program after all the experimental data have been read and processed.

4

```
// JOB                    S71007,S51


// FOR
* LIST SOURCE PROGRAM
*IOCS(CARD, 1132 PRINTER)

C      CONFRONTATION OF DATA AND MODEL.  A NUMERICAL  COMPARISON
C      TITRATION CURVE
C      MONOPROTIC ACID, ASSUMED VALUE OF KHA

C      DATA CARDS HAVE VMOH PUNCHED WITHIN THE FIRST 20 SPACES AND
C      PH PUNCHED WITHIN THE SECOND 20 SPACES
C      INCLUDE DECIMAL POINT IN EACH VALUE OF VMOH AND PH
C      LAST DATA CARD MUST HAVE A NEGATIVE VALUE OF VMOH

       REAL KHA, KW, NUM, MHA, MMOH
       KHA = 1.75E-5
       VHA = 25.00
       MHA = 0.1000
       MMOH = 0.1000
       KW = 1.008E-14

   28  READ (2,25) V, PH
   25  FORMAT (F20.2, F20.2)
       IF (V) 30, 29, 29
   29  H = 10**(-PH)
       NUM = H**3 + KHA*(H**2) - (KW + (KHA*MHA))*H - KW*KHA
       DEN =  H**3 + (KHA + MMOH)*(H**2) + (KHA*MMOH - KW)*H - KW*KHA
       VMOH = -VHA*NUM/DEN
       WRITE (3,10) PH, VMOH, V
   10  FORMAT (1X,'PH  =',F6.2,4X,'VMOH (CAL)  =',F7.2,4X,'VMOH (EXP)  ='
      *,F7.2)
       GO TO 28
   30  CALL EXIT
       END

// XEQ
```

PRINTER OUTPUT:

```
PH  =  3.42    VMOH (CAL)  =    1.00    VMOH (EXP)  =    1.00
PH  =  4.11    VMOH (CAL)  =    4.57    VMOH (EXP)  =    4.47
PH  =  4.51    VMOH (CAL)  =    9.02    VMOH (EXP)  =    8.89
PH  =  4.58    VMOH (CAL)  =    9.97    VMOH (EXP)  =   10.26
PH  =  4.85    VMOH (CAL)  =   13.82    VMOH (EXP)  =   14.53
PH  =  4.96    VMOH (CAL)  =   15.36    VMOH (EXP)  =   15.96
PH  =  5.32    VMOH (CAL)  =   19.62    VMOH (EXP)  =   19.42
PH  =  5.54    VMOH (CAL)  =   21.46    VMOH (EXP)  =   21.19
```


6~

In actual practice, we would run this program several times, each time with a different value of KHA. The "best" value of the equilibrium constant would be the value that gave the best fit of experimental and calculated values of titrant volume.

EXERCISES

1. Certain regions of the simulated titration curve, calculated with programs such as 1, 2, 3, or 4, are markedly more sensitive to the particular value of the equilibrium constants than other regions. Determine, by running such a program with a range of equilibrium constant values, what experimental data will be most useful in determining the best value of K_{HA}.

2. The computer can be helpful in making a decision about which, of several sets of output volumes in program 4, represents the best fit of data and model. One criterion for best fit might be that, in the range where the calculated curve is most sensitive to changes in the value of the equilibrium constant, the differences between calculated and experimental values of volumes should be as small as possible. Thus we might find a program that made such a subtraction, and printed out the difference, to be helpful. Even more helpful would be a program that summed the absolute values (or the squares) of these differences, and printed this sum at the end of the calculations. Write such a program, and execute it with your data, and with several values of an equilibrium constant.

A GRAPHICAL COMPARISON OF DATA AND THE PREDICTIONS OF A MODEL

FORTRAN Program 5 takes the experimental data from a titration experiment, punched on cards in the same format as required by program 4, and plots these data on the same graph as a calculated plot of the predictions of the chemical model. When such comparisons are made for

several different values of an equilibrium constant, inspection of the computer-drawn graphs may be sufficient to permit an informed estimate of the best equilibrium constant value.

The graphical output from this program gives the prediction of the chemical model as a smooth curve, and the experimental data as points plotted on the same graph. Such output, using the same data cards as used for demonstrating program 4, is presented on page 46. The model and the data are consistent if the points fit the curve within the limits of the experimental uncertainty of the data.

• *What is an explanation of each of the following deviations between plotted points and calculated curve?*

¶ The data points lie above the curve for volumes between 5 and 20 ml for a titration curve that has a sharp inflection point at about 25 ml.

¶ The data points lie below the curve for volumes between 5 and 20 ml.

¶ The data points lie to the right of the curve for pH values from 7 to 10.

¶ The data points lie below the curve for volumes greater than 30 ml.

¶ The data points lie randomly above and below the curve for volumes between 5 and 20 ml.

SOME NOTES ON THE COMPUTER PLOTTING PROGRAM

The smooth solid curves drawn by the plotter are in fact constructed by instructing the plotter to draw a series of very short connected straight line segments. The procedure is to bring the pen to one end of the desired line, with the pen up (lifted off the paper) so that the

5

```
// JOB                S71007,S51


// FOR
*ONE WORD INTEGERS
* LIST SOURCE PROGRAM
*IOCS(CARD, 1132 PRINTER, TYPEWRITER, PLOTTER)
C      TITRATION CURVE

C      COMPARISON OF EXPERIMENTAL DATA WITH THE PREDICTIONS OF A
C      CHEMICAL MODEL

C      MONOPROTIC ACID, ASSUMED VALUE OF KHA

C      DATA CARDS HAVE VMOH PUNCHED WITHIN THE FIRST 20 SPACES
C      DATA CARDS HAVE PH PUNCHED WITHIN THE SECOND 20 SPACES
C      INCLUDE DECIMAL POINT IN EACH VALUE OF VMOH AND PH
C      LAST DATA CARD MUST HAVE A NEGATIVE VALUE OF VMOH

       REAL KHA, KW, NUM, MHA, MMOH
       KHA = 1.75E-5
       VHA = 25.00
       MHA = 0.1000
       MMOH = 0.1000
       KW = 1.008E-14
       CALL PREP (.2, .55, 1., 1.)
       WRITE (7,15) KHA
   15 FORMAT ('CONFRONTATION OF CHEMICAL MODEL WITH TITRATION DATA, KHA
     X =',E11.3)

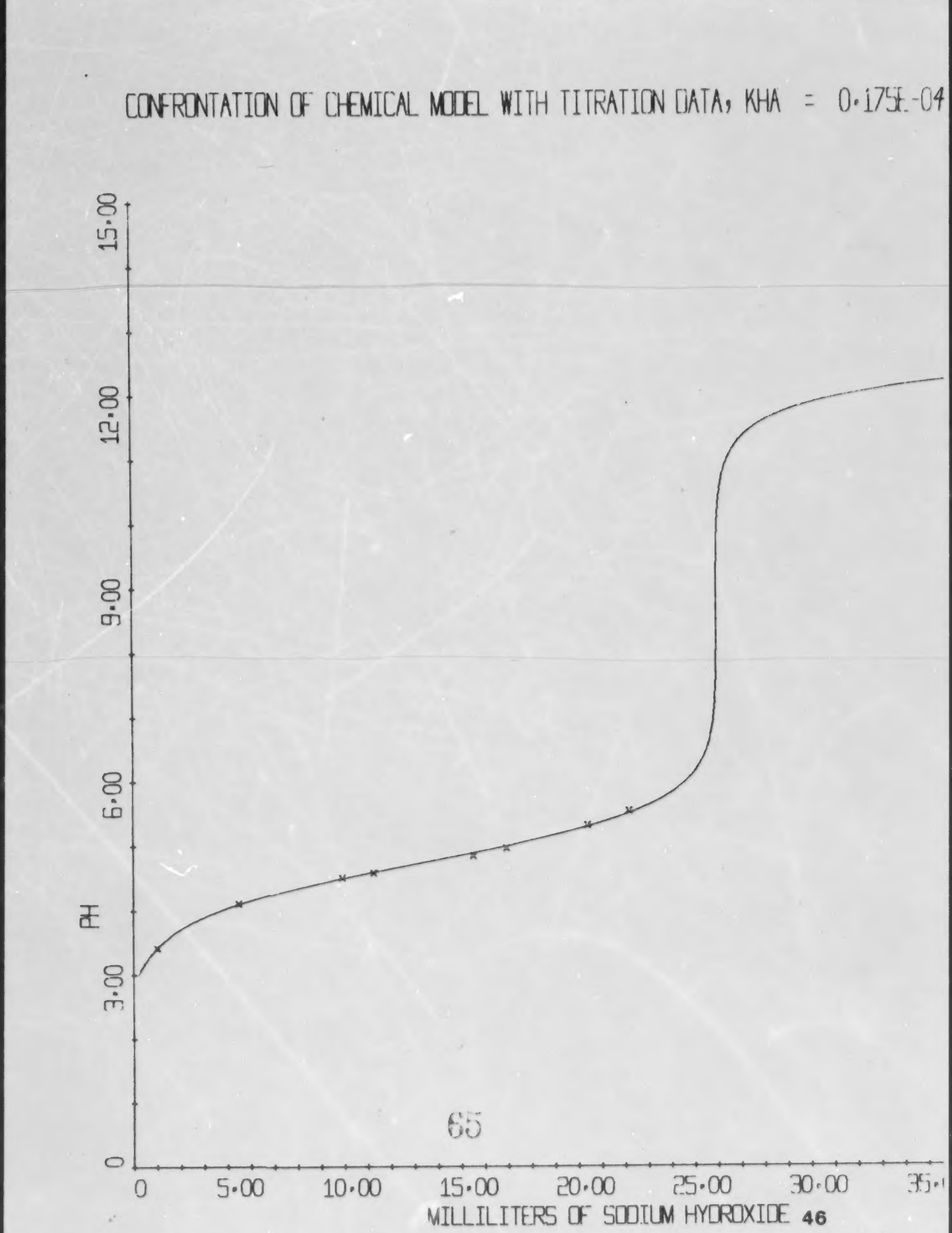
C      CALCULATION AND PLOTTING OF THE TITRATION CURVE
       H = 1.
     1 H = .5*H
       PH = -(ALOG(H))/2.303
       NUM = H**3 + KHA*(H**2) - (KW + (KHA*MHA))*H - KW*KHA
       DEN =  H**3 + (KHA + MMOH)*(H**2) + (KHA*MMOH - KW)*H - KW*KHA
       VMOH = -VHA*NUM/DEN
       IF (VMOH) 1,2,2
     2 CALL FPLOT (-2,VMOH,PH)
     5 H = H - .1*H
       PH = -(ALOG(H))/2.303
       DEN =  H**3 + (KHA + MMOH)*(H**2) + (KHA*MMOH - KW)*H - KW*KHA
       NUM = H**3 + KHA*(H**2) - (KW + (KHA*MHA))*H - KW*KHA
       VMOH = -VHA*NUM/DEN
       IF(50.-VMOH) 10,3,3
     3 CALL FPLOT (0,VMOH,PH)
       GO TO 5

C      PLOTTING DATA POINTS FROM THE TITRATION
    10 CONTINUE
    28 READ (2,25) V,P
    25 FORMAT (F20.2,F20.2)
       IF (V) 30,29,29
    29 CALL FPLOT (1,V,P)
       CALL FPLOT (-2,V,P)
```

```
      CALL POINT (1)
      GO TO 28

C     DRAWING AND LABELLING THE AXES
   30 CALL YAXIS (0., 0., 1., 15, 5)
      WRITE (7,17)
   17 FORMAT ('PH')
      CALL XAXIS (0.,0.,1.,50,10)
      WRITE (7,16)
   16 FORMAT ('MILLILITERS OF SODIUM HYDROXIDE')
      CALL FINPL
      CALL EXIT
      END
```

```
// XEQ
```


CONFRONTATION OF CHEMICAL MODEL WITH TITRATION DATA, KHA = 0.175E-04
15.00
12.00
9.00
6.00
3.00
0
PH
0
5.00
10.00
15.00
20.00
25.00
30.00
MILLILITERS OF SODIUM HYDROXIDE

pen is not writing. The pen is then lowered. When the pen is then moved in the down position to the other end of the desired line, the straight line is drawn. An instruction to move to another position yields a continuation of the line if the pen is left in the down position. The necessary information to control these pen movements is included in the computer program in the form of FPLOT statements of the form

```
CALL FPLOT (I,X,Y)
```

where I is an integer that controls the up-down pen position as follows:

I = 0	⇒	no change
I = positive	⇒	control pen before movement
I = negative	⇒	control pen after movement
I = odd	⇒	raise pen away from paper
I = even	⇒	lower pen to writing position

The variables X and Y are the coordinates of the graph position to which the pen is moved.

If you want to place a printed label on the graph, use the FPLOT statement to bring the pen to the position where you wish the lower left corner of the first character to appear. The pen should be in the up position. Then use the statement

```
WRITE (7,J)
```

where J is the number of a FORMAT statement of the form

```
J FORMAT ('        ')
```

The desired letters and numerals for the label go between the ' ' marks.

If you want to plot a point on the graph, you may use the

statement

```
CALL POINT (1)
```

This statement causes the plotter to draw an × mark at the current pen position. It expects to find the pen down and it leaves the pen down when finished. Other numbers may be used in this statement, with other marks resulting; details are given in the IBM plotter manual.

At the end of a graph, when all plotting and graphing is finished, it is convenient to use the statement

```
CALL FINPL
```

This subroutine plots a cross at the lower left hand corner on top of a plus sign put there by PREP. This is a check on machine errors during the plotting. If the two symbols do not land exactly on top of each other, the graph should not be trusted. FINPL then raises the pen and moves it to an appropriate position for beginning a new graph.

USE OF THE MACROSCOPIC HALF-EQUIVALENCE METHOD FOR MAKING AN INFORMED GUESS OF THE VALUE OF THE EQUILIBRIUM CONSTANT FOR A MONOPROTIC ACID

In order to confront the data from a titration experiment with the predictions of a particular chemical model, it is necessary to assume some specific numerical value for the equilibrium constant K_{HA}. Only then can a theoretical titration curve be calculated for direct comparison with the experimental curve. If the agreement is not very good, then a different value for K_{HA} can be tried. This trial-and-error approach — the method of successive approximations — will usually yield a "best value" of K_{HA} after three or four such

calculations if the first trial value of K_{HA} is reasonably close to the value that finally gives the best fit between chemical model and experimental data. With a computer being used for these calculations, almost all the effort goes into the first calculation. Succeeding calculations, with different trial values of K_{HA}, require only that you change a single card in the program deck, and each calculation takes only about five minutes of IBM 1130 computer time. We have already seen how to perform the calculations and get a readout, on the plotter, of the simulated titration curve plotted together with experimental data points obtained from an actual laboratory titration. What we need now is a simple way to make a good guess for a value of K_{HA} to begin the successive approximations process.

During the titration of a monoprotic acid, the pH value of the solution will be equal numerically to the pK_{HA} of the acid when the concentrations of species HA and A^- are equal. The criterion of equal concentrations of these two species is the *microscopic definition of the half-equivalence point of the titration*. A *macroscopic half-equivalence point* is often defined as the point in the titration at which a volume of base has been added which is equal to half that volume required for reaching the equivalence point.

Microscopic and macroscopic half-equivalence points are not necessarily identical. If they are the same, within the limits of experimental errors of measurement of volume and pH, then the pH value at the macroscopic half-equivalence point provides the datum for a convenient determination of pK_{HA} and therefore of K_{HA}. In any event, the determination of the pH at the macroscopic half-equivalence point provides a convenient and straight-forward way to

get an approximate value of K_{HA} to serve as a starting point for the successive approximations calculations. The K_{HA} so obtained will be an excellent approximation for cases in which the actual value of the dissociation constant lies between 10^{-4} and 10^{-10} — where the actual value of pK_{HA} lies between 4 and 10. Even when K_{HA} is of the order of 10^{-2}, the value given by the half-equivalence method is a useful starting point for a series of successive approximations.

FORTRAN Program 6 enables us to evaluate the half-equivalence method by simulating the titrations of acids with K_{HA} values ranging from 10^{-1} to 10^{-12}. The resulting computer-produced plots are presented on pages 53 to 58. For each of these simulations, a straight line is drawn with $pH = pK_{HA}$, and another with $V_{MOH} = \frac{1}{2}V_{MOH,equivalence}$. If the intersection of these two lines lies on the calculated titration curve, the macroscopic and microscopic half-equivalence points coincide. All these calculations are for titrations in which both acid and titrant have concentrations of 0.1 moles per liter. The half-equivalence method becomes less reliable at lower concentrations, but the loss of accuracy at $pK_{HA} = 4$ is not very dramatic at concentrations of 0.01 molar, for instance.

SOME NOTES ON THE COMPUTER PROGRAM

The titration curve for an acid with a large value of the dissociation constant — that is, for a relatively strong acid — begins with a slope close to zero. An aqueous solution of a strong acid is a good buffer solution. This fact introduces a strange feature into these computer plots that is entirely a quirk of our programming: the calculated titration curve doesn't necessarily begin at $V_{MOH} = 0$! The problem is that in the

6

```
// JOB                    S71007,S51


// FOR
*ONE WORD INTEGERS
* LIST SOURCE PROGRAM
*IOCS(CARD, 1132 PRINTER, TYPEWRITER, PLOTTER)
C       TEST OF THE VALIDITY OF THE HALF-EQUIVALENCE METHOD
C       FOR EVALUATING THE EQUILIBRIUM CONSTANT

C       MONOPROTIC ACID

        REAL KHA, KW, NUM, MHA, MMOH
        KHA = 1.E-4
        VHA = 25.00
        MHA = 0.1000
        MMOH = 0.1000
        KW = 1.008E-14
        CALL PREP (.2, .55, 1., 1.)
        WRITE (7,15) KHA
   15 FORMAT ('TEST OF THE HALF-EQUIVALENCE METHOD, KHA = ',E9.2)

C       MARKING OF THE HALF-EQUIVALENCE VOLUME, AND PH = PKHA
        VMOH = .5*VHA*MHA/MMOH
        PH = -(ALOG(KHA))/2.303
        VMOH 1 = VMOH - 3.
        VMOH2 = VMOH + 3.
        PH1 = PH - 1.
        PH2 = PH + 1.
        CALL FPLOT(1,VMOH,PH1)
        CALL FPLOT(-2,VMOH,PH1)
        CALL FPLOT(-2,VMOH,PH2)
        CALL FPLOT(1,VMOH1,PH2)
        CALL FPLOT(-2,VMOH1,PH)
        CALL FPLOT(-1,VMOH2,PH)

C       CALCULATION AND PLOTTING OF THE TITRATION CURVE
        H = 1.
    1   H = .5*H
        PH = -(ALOG(H))/2.303
        NUM = H**3 + KHA*(H**2) - (KW + (KHA*MHA))*H - KW*KHA
        DEN =  H**3 + (KHA + MMOH)*(H**2) + (KHA*MMOH - KW)*H - KW*KHA
        VMOH = -VHA*NUM/DEN
        IF (VMOH) 1,2,2
    2   CALL FPLOT (-2,VMOH,PH)
    5   H = H - .1*H
        PH = -(ALOG(H))/2.303
        DEN =  H**3 + (KHA + MMOH)*(H**2) + (KHA*MMOH - KW)*H - KW*KHA
        NUM = H**3 + KHA*(H**2) - (KW + (KHA*MHA))*H - KW*KHA
        VMOH = -VHA*NUM/DEN
        IF(50.-VMOH) 10,3,3
    3   CALL FPLOT (0,VMOH,PH)
        GO TO 5

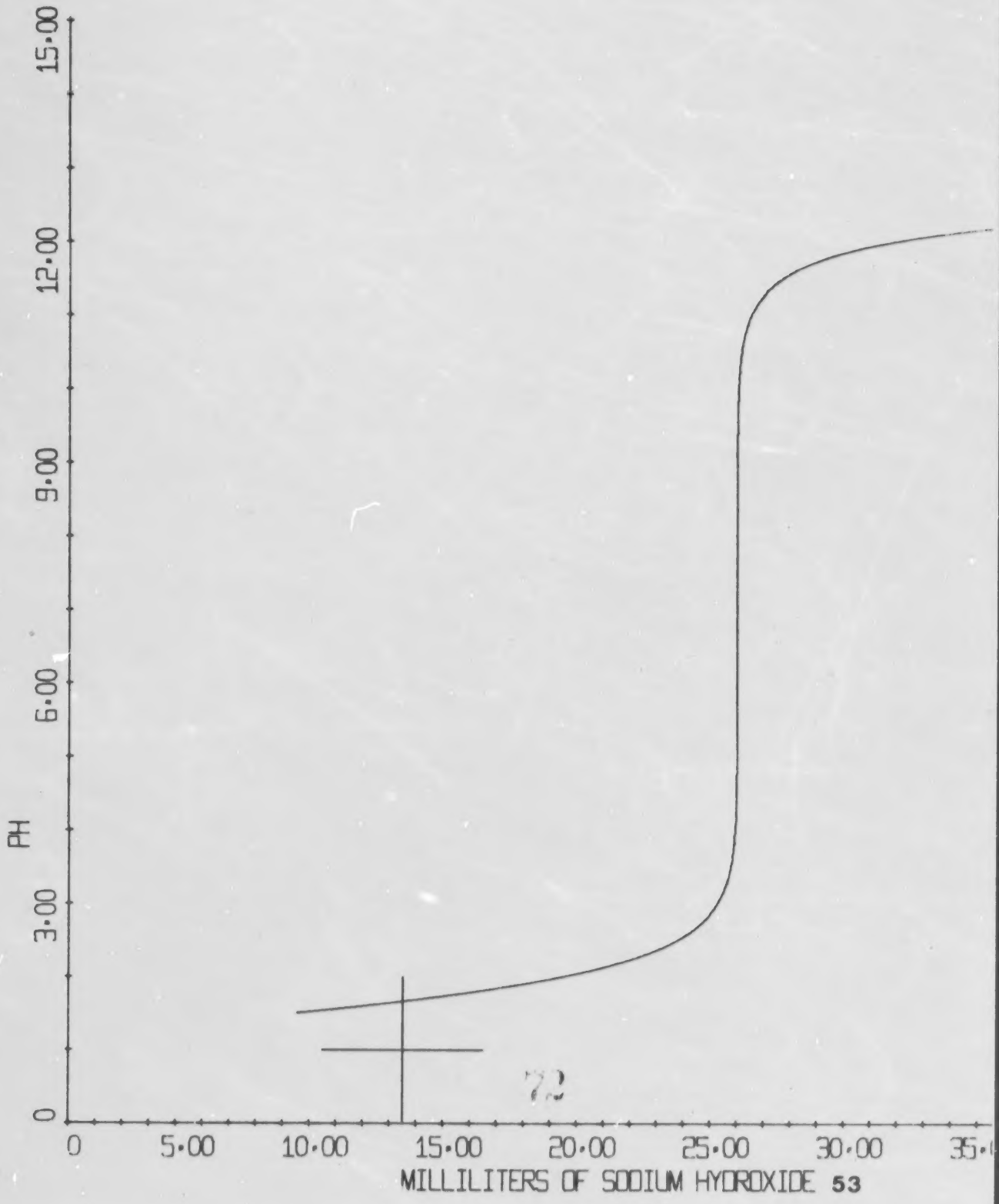
C       DRAWING AND LABELLING THE AXES
```

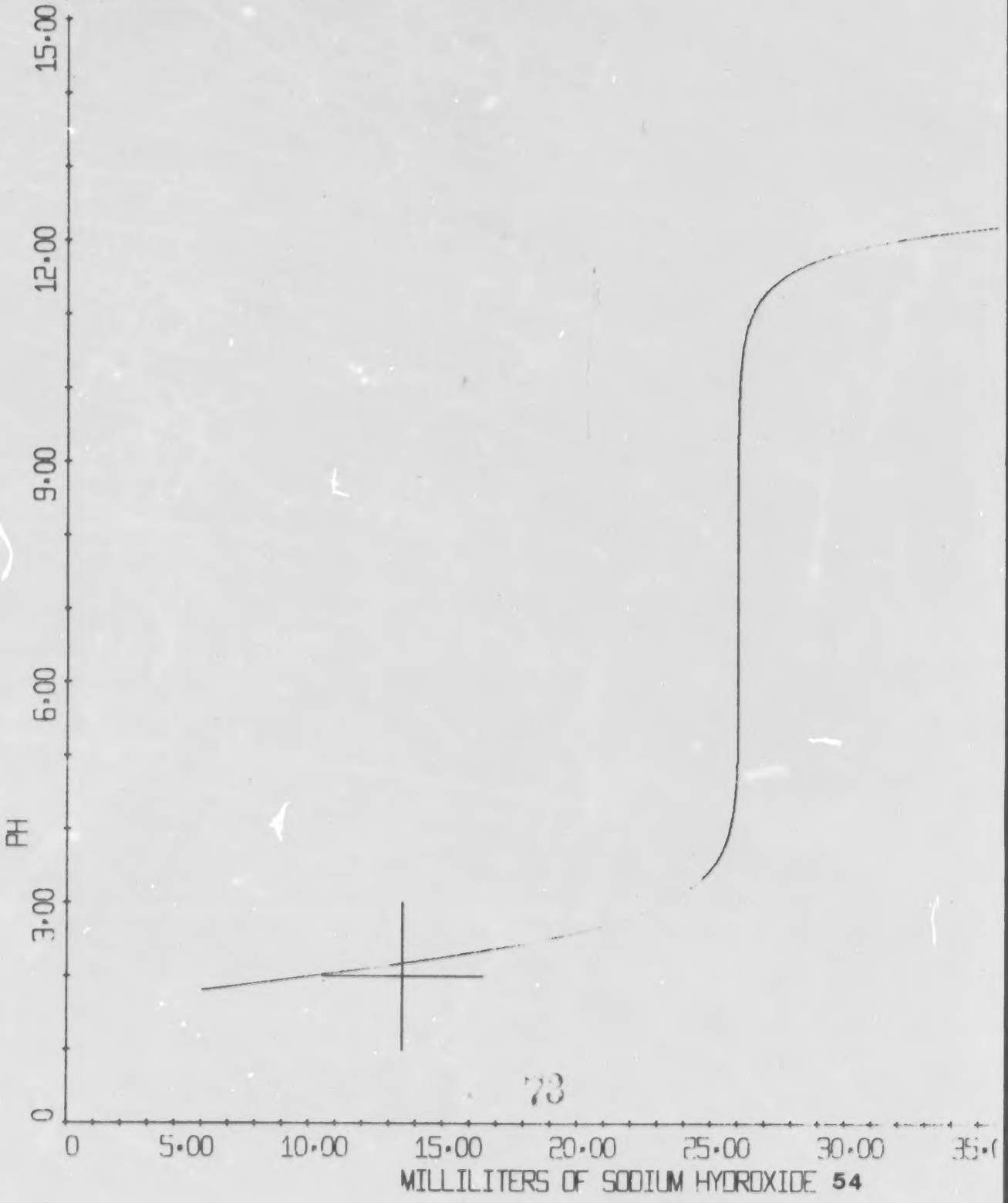
```
PAGE   2

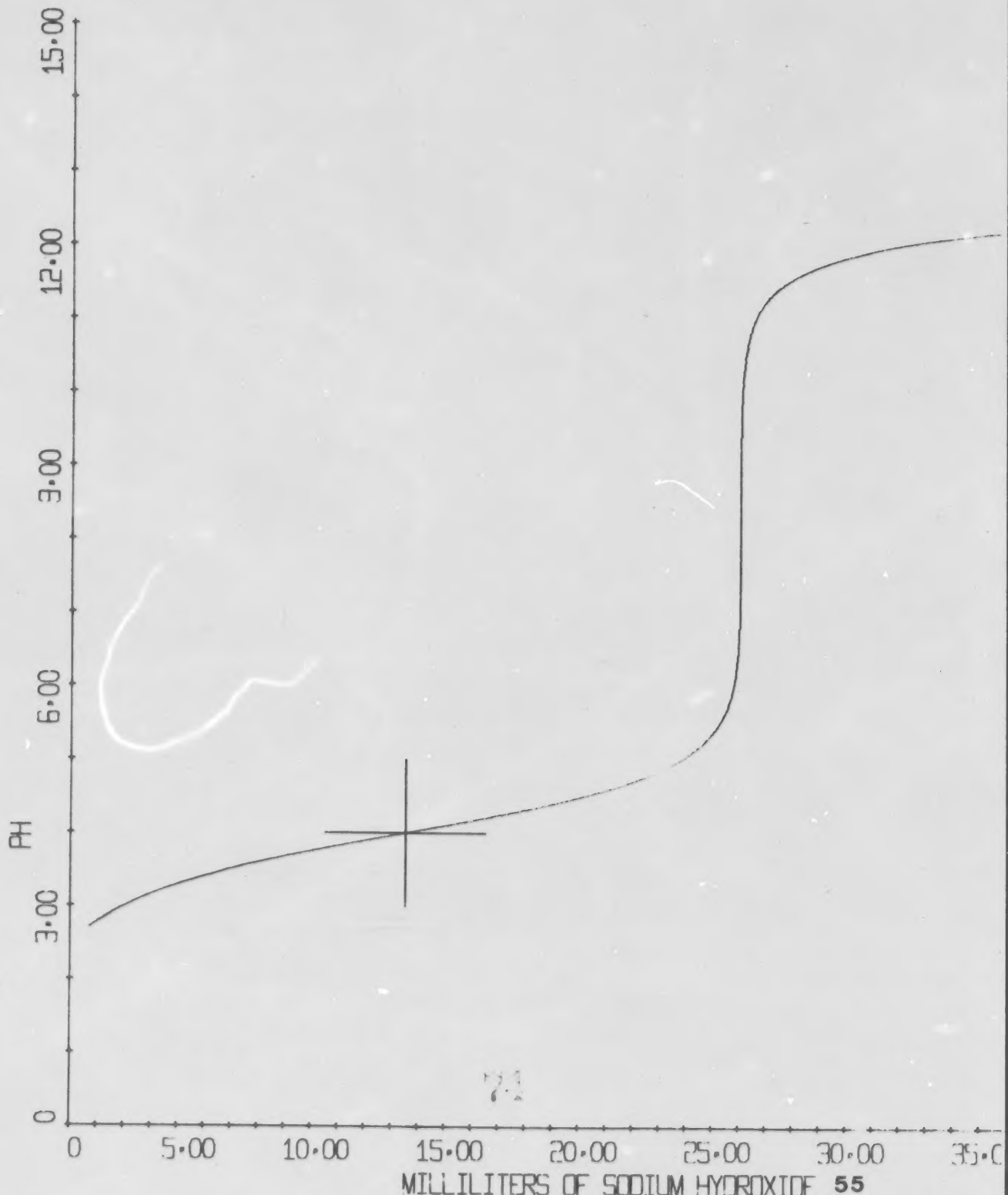
10     CALL YAXIS (0.,0.,1.,15,5)
       WRITE (7,17)
   17 FORMAT ('PH')
       CALL XAXIS (0.,0.,1.,50,10)
       WRITE (7,16)
   16 FORMAT ('MILLILITERS OF SODIUM HYDROXIDE')
       CALL FINPL
       CALL EXIT
       END

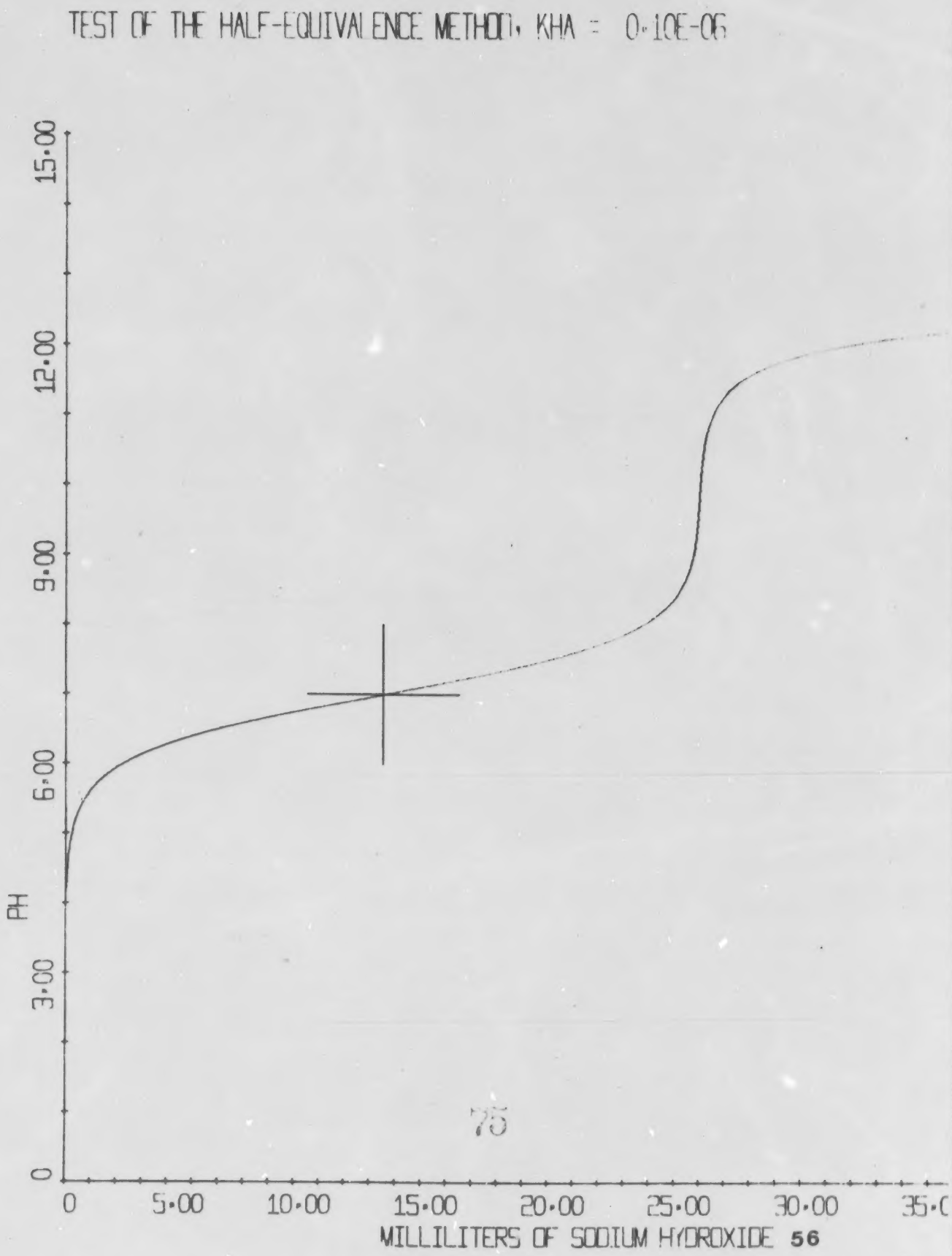


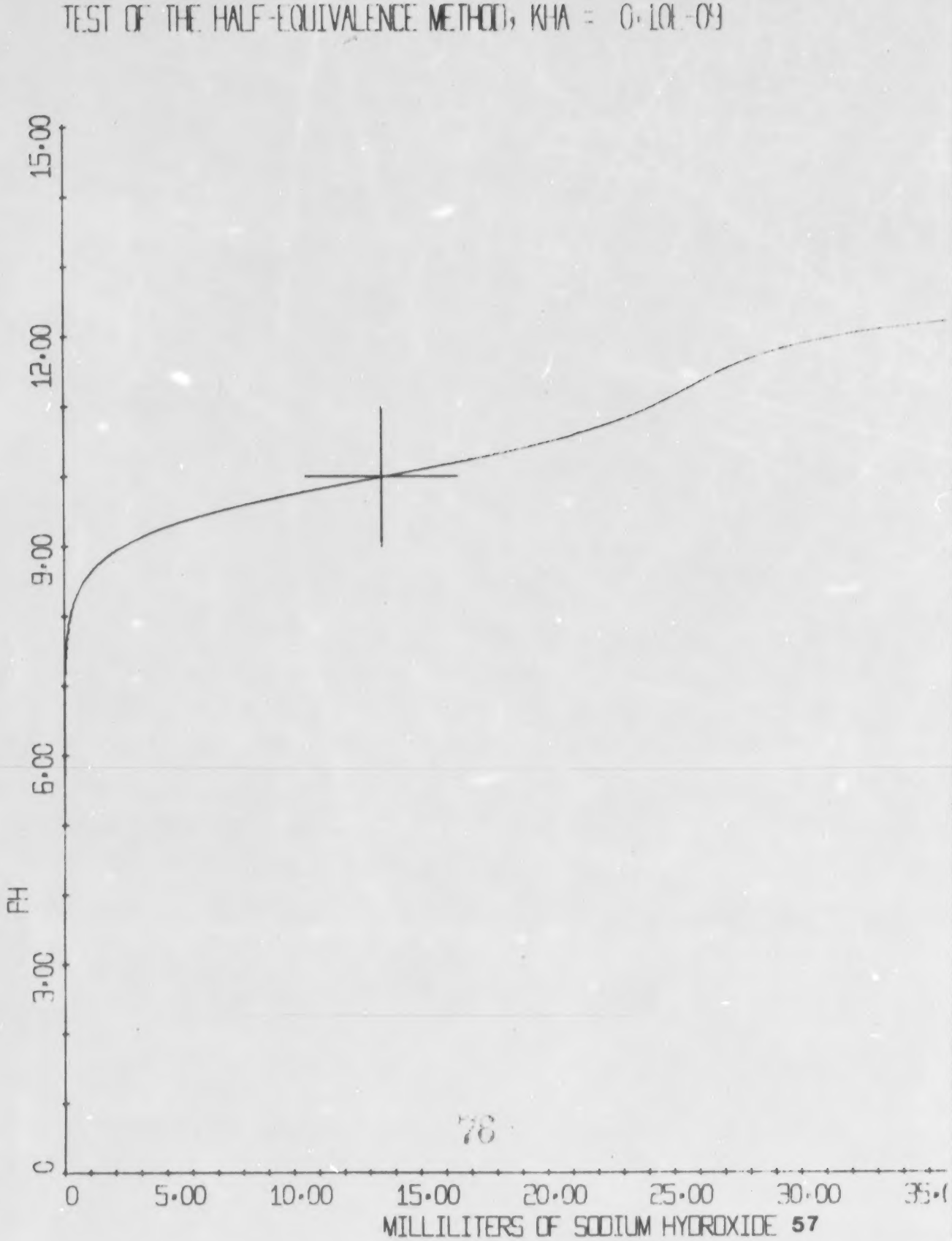
// XEQ
```

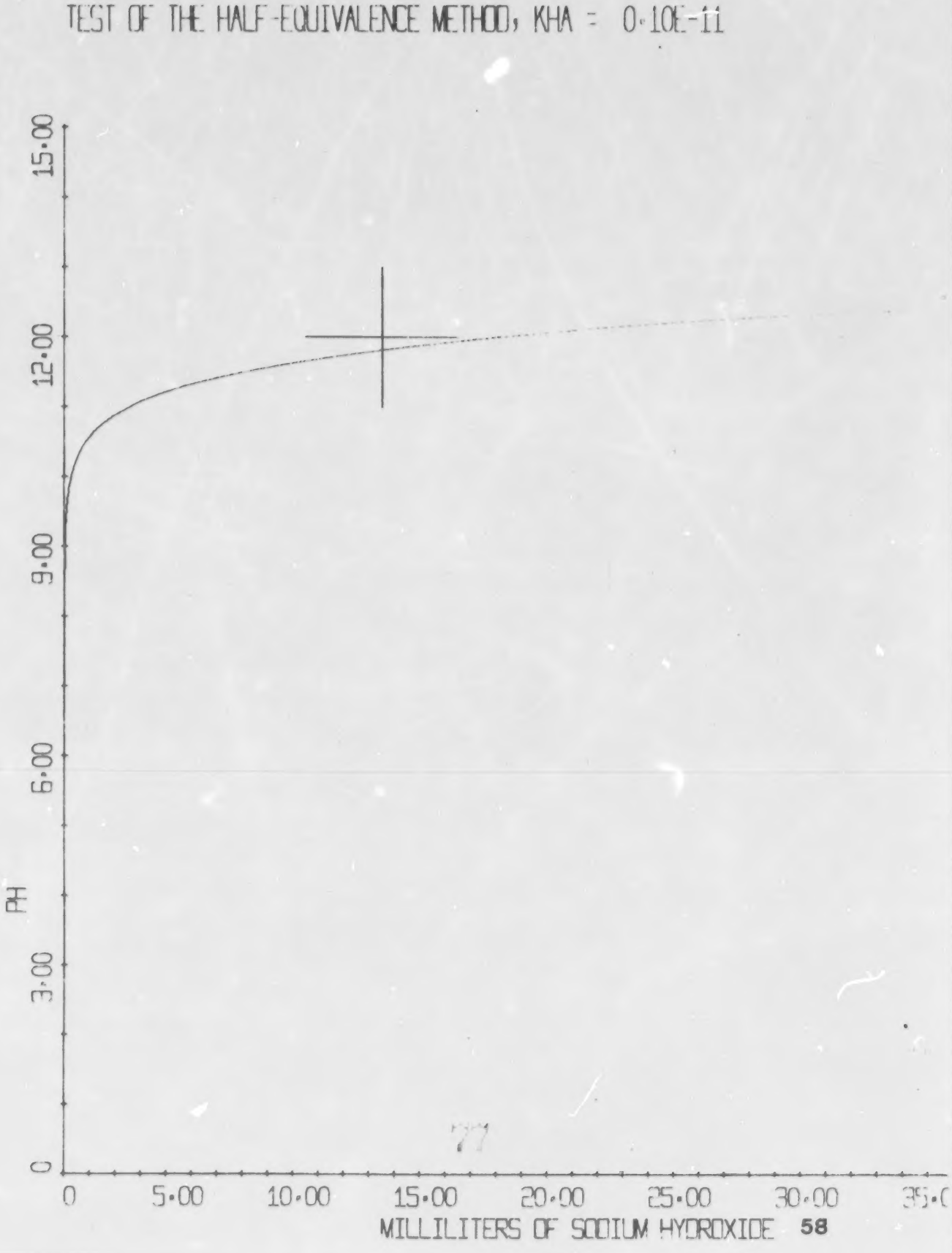

TEST OF THE HALF-EQUIVALENCE METHOD; KHA = 0.10E 00
15.00
12.00
9.00
6.00
3.00
0
PH
0
5.00
10.00
15.00
20.00
25.00
30.00
MILLILITERS OF SODIUM HYDROXIDE


TEST OF THE HALF-EQUIVALENCE METHOD, KHA = 0.10E-01
15.00
12.00
9.00
6.00
3.00
0
PH
0
5.00
10.00
15.00
20.00
25.00
30.00
MILLILITERS OF SODIUM HYDROXIDE


TEST OF THE HALF-EQUIVALENCE METHOD, KHA = 0.10E-03
15.00
12.00
9.00
6.00
3.00
0
PH
0
5.00
10.00
15.00
20.00
25.00
30.00
MILLILITERS OF SODIUM HYDROXIDE


TEST OF THE HALF-EQUIVALENCE METHOD, KHA = 0.10E-06
15.00
12.00
9.00
6.00
3.00
0
PH
0
5.00
10.00
15.00
20.00
25.00
30.00
35.0
MILLILITERS OF SODIUM HYDROXIDE


TEST OF THE HALF-EQUIVALENCE METHOD, KHA = 0.10E-03
15.00
12.00
9.00
6.00
3.00
0
PH
0
5.00
10.00
15.00
20.00
25.00
30.00
MILLILITERS OF SODIUM HYDROXIDE


TEST OF THE HALF-EQUIVALENCE METHOD, KHA = 0.10E-11
15.00
12.00
9.00
6.00
3.00
0
PH
0
5.00
10.00
15.00
20.00
25.00
30.00
MILLILITERS OF SODIUM HYDROXIDE

searching process at the beginning of the calculations, when the program is looping until V_{MOH} becomes positive, the pH increment is too large. It is possible for an overshoot of almost 0.5 pH units to occur. This is of no consequence for a weak acid, where the titration curve begins with a rather steep slope. The simple remedy for this problem (if you consider it to be a problem) is to reduce the pH increment to some smaller value by modifying one statement in the program.

The section of the program for drawing the two intersecting lines contains some strange instructions in the form of the FPLOT statements. The procedure is to bring the pen to one end of the desired line, with the pen up so that the pen is not writing. The pen is then lowered, and moved while in the down position to the other end of the desired line. This process yields a straight-line segment. The necessary information for decoding these FPLOT instructions is given on page 47.

A METHOD OF ESTIMATING THE VALUE OF K_W FROM AN INSPECTION OF THE TITRATION CURVE

Confrontation of data and model also requires that you assume some specific numerical value for the equilibrium constant K_w. Then a series of successive approximations can be used to find the value that gives the best fit between calculations and titration data. A straightforward method of estimating the value of K_w involves use of Equation 7:

$$K_w = (H^+)(OH^-)$$

A place on the titration curve is needed where you can know the

values of both (H^+) and (OH^-).

If you continue the titration well past the equivalence point, you will find that the pH approaches a limiting value. This limiting value is the pH of the titrant. Eventually, if you were to add an extremely large volume of titrant, the resulting solution would be essentially pure titrant. If you can make a reliable estimate of the limiting pH value, then you can use Equation 7 to calculate K_w. This pH value is converted into a concentration, giving the value of (H^+) that results when (OH^-) is equal to M_{NaOH}.

Rather than to rely on guessing the value of this limiting pH, you may find that it is more convenient to measure the pH of the pure titrant solution.

WHERE TO FIND EQUILIBRIUM-CONSTANT VALUES IN THE LIBRARY

Much quantitative information about chemical reactions has been reported in research articles in the form of numerical values of equilibrium constants. Such numbers for acid-base reactions have been collected in several useful compilations that are listed and described in this bibliography. Obviously, research results reported after a set of tables has been compiled will not appear in those tables. For recent research, consult Chemical Abstracts or Chemical Titles for references to the original research papers.

GENERAL TABULATIONS

L. G. Sillén and A. E. Martell, Stability Constants of Metal-Ion Complexes, 2nd ed., London: The Chemical Society, 1964. Supplement, 1971.

An excellent and reliable source of equilibrium constant values. For each entry, there is information about the solvent, ionic strength, temperature, and experimental method, together with a reference to the original research report. This is a virtually complete survey of the chemical literature for acid-base reactions, metal-ligand reactions, inorganic oxidation-reduction reactions, and precipitation reactions.

ACID-BASE REACTIONS

D. D. Perrin, Dissociation Constants of Inorganic Acids and Bases in Aqueous Solution, London: Butterworths, 1969.

D. D. Perrin, Dissociation Constants of Organic Bases in Aqueous Solution, London: Butterworths, 1965

G. Kortüm, W. Vogel, and K. Andrussow, Dissociation Constants of Organic Acids in Aqueous Solution, London: Butterworths, 1961.

Each of these volumes was published under the auspices of the International Union of Pure and Applied Chemistry. Complete information regarding solvent, temperature, experimental method, data treatment, and a reference to the primary research publication is given for every entry.

USE OF A VISUAL INDICATOR TO DETECT THE EQUIVALENCE POINT IN A TITRATION

Thus far in this case study, we have been considering the use of titration data to learn about the chemical nature of a carboxylic acid in water solution. The most common use of the burette is in the titration of solutions to determine the quantities of some material in those solutions. Such titrations are among the most convenient methods of *quantitative volumetric analysis*, and depend for their reliability upon methods of detecting the titration equivalence point. For determining the amount of a carboxylic acid in a water solution, the color change of an acid-base indicator is especially convenient. We shall use a computer simulation to investigate the utility and the limitations of visual equivalence-point detection in the titration of a monoprotic acid.

Let us examine a solution prepared by mixing aqueous solutions of the weak acid HA, the strong base NaOH, and the indicator HI. Visual detection of the equivalence point depends on the species HI and I^- having markedly different colors, with at least one of those species being highly colored so that only trace quantities of the indicator are needed in solution.

> Often it is necessary to dissolve the indicator in an alcohol-water mixture in order to get enough indicator into a drop of indicator solution. However, in describing the chemistry of a titration, it is customary to ignore the drop of alcohol that is introduced into the titration mixture when the indicator solution is added.

We shall examine the conditions under which an abrupt color change would be expected to coincide with the equivalence point, thus signalling the point to halt the titration and read the burette.

Consider the special case of a titration in which the indicator concentration is so low that throughout the titration (but in particular in the vicinity of the equivalence point)

$$(I^-) << (A^-) \tag{15}$$

If

$$K_{HI} < K_{HA} \tag{16}$$

the inequality 15 will be satisfied if

$$[I] << [A] \tag{17}$$

It is often quite easy to arrange experimental conditions so that conditions 15, 16, and 17 are satisfied.

The relevant equilibria and associated equilibrium constant equations that we need for constructing a model for this system are

$$H_2O \rightleftarrows H^+ + OH^- \qquad K_w = (H^+)(OH^-) \tag{18}$$

$$HA \rightleftarrows H^+ + A^- \qquad K_{HA} = \frac{(H^+)(A^-)}{(HA)} \tag{19}$$

$$HI \rightleftarrows H^+ + I^- \qquad K_{HI} = \frac{(H^+)(I^-)}{(HI)} \tag{20}$$

The algebraic equations for conservation of mass are

$$[A] = (HA) + (A^-) \tag{21}$$

$$[Na] = (Na^+) \tag{22}$$

$$[I] = (HI) + (I^-) \tag{23}$$

The electroneutrality relationship is

$$(H^+) + (Na^+) = (A^-) + (OH^-) + (I^-) \tag{24}$$

The volume variables that tie our description directly to burette readings in a titration can be introduced into the model via the three equations

$$[A] = \frac{V_{HA}M_{HA}}{V_{HI} + V_{HA} + V_{NaOH}} \tag{25}$$

$$[Na] = \frac{V_{NaOH}M_{NaOH}}{V_{HI} + V_{HA} + V_{NaOH}} \tag{26}$$

$$[I] = \frac{V_{HI}M_{HI}}{V_{HI} + V_{HA} + V_{NaOH}} \tag{27}$$

where V_{HA} is the volume of acid solution (of molarity M_{HA}) that was originally placed in the titration vessel, V_{HI} is the volume of indicator solution (of molarity M_{HI}) added, and V_{NaOH} is the volume of titrant (of molarity M_{NaOH}) which has been delivered from the burette at a given point in the titration. Only V_{NaOH} is a variable during a particular titration.

With approximation 15 introduced, Equation 24 becomes

$$(H^+) + (Na^+) = (A^-) + (OH^-) \tag{28}$$

Equations 18, 19, 21, 22, 25, 26, 27, and 28 can be combined to give

$$V_{NaOH} = \frac{-V_{HA}\begin{bmatrix}(H^+)^3 + K_{HA}(H^+)^2 \\ -\{K_{HA}M_{HA} + K_w\}(H^+) \\ -K_wK_{HA}\end{bmatrix} - V_{HI}\begin{bmatrix}(H^+)^3 + K_{HA}(H^+)^2 \\ -K_w(H^+) \\ -K_wK_{HA}\end{bmatrix}}{(H^+)^3 + \{K_{HA} + M_{NaOH}\}(H^+)^2 + \{K_{HA}M_{NaOH} - K_w\}(H^+) - K_wK_{HA}} \tag{29}$$

Equation 29 contains no reference to either HI or I^- as chemical species; the volume of indicator solution appears, but this solution functions in Equation 29 only to increase the total volume of the titrated solution, thus slightly diluting the solution. The requirement that [I] be small has resulted in separation of variables. The indicator plays no role *in establishing* the value of (H^+) for

any value of added titrant. The distribution of total I between the species HI and I^- depends solely on the value of (H^+). Thus we see that this concentration variable (H^+) functions as a *master variable*, providing the chemical coupling between equilibria 18, 19, and 20, and providing the algebraic coupling between Equation 20 and the rest of the mathematical model.

We shall now proceed to make a quantitative prediction for the color change of the indicator in a titration. Quantitative measurement of color changes in solution is best made in terms of the optical *absorbance*, A, of the solution at some appropriate wavelength. Absorption of visible light by either of the two indicator species occurs when a photon of light is absorbed by electrons in the anion or the molecule. Association or dissociation of the proton changes the permitted wavelengths of light that can be absorbed by the indicator species. The result is a change in the color of the solution containing the indicator. We are interested in *how much* light is absorbed by the solution. This change in the amount of light of each wavelength absorbed by the solution as the titration proceeds is directly related to the variation in concentrations of the chemical species in solution.

A beam of monochromatic light will be reduced in intensity while passing through a solution that contains chemical species which absorb photons of that wavelength. The decrease in intensity depends on the number of molecules of the absorbing species in the path of the light beam. If the beam has an intensity I_0 before entering the solution, emerging from the solution with an intensity I, then the Bouger-Beer Law states that, for a solution containing

only a single absorbing species X,

$$I = I_0 10^{-\ell\varepsilon_X(X)} \qquad (30)$$

where ℓ is the optical pathlength, the distance travelled through the solution by the light beam; (X) is the molar concentration of chemical species X; and ε_X is a proportionality constant, called the molar absorptivity of species X.

If there are two different absorbing species in solution, then Equation 30 is modified to become

$$I = I_0\left[10^{-\ell\varepsilon_{X_1}(X_1)}\right]\left[10^{-\ell\varepsilon_{X_2}(X_2)}\right] \qquad (31)$$

Species X_1 and X_2 are here assumed to absorb light independently of one another. Equation 31 can be written in the equivalent form

$$I = I_0 10^{-\ell\{\varepsilon_{X_1}(X_1) + \varepsilon_{X_2}(X_2)\}} \qquad (32)$$

To get from Equation 31 to Equation 32, use was made of the relationship

$$\{10^a\}\{10^b\} = 10^{\{a+b\}}$$

Quantitative measurements of light absorption in solution are conveniently made in the laboratory with an optical absorption spectrophotometer, and the measurements are usually reported in terms of either transmittance, T, or absorbance, A. Transmittance is defined by

$$T \equiv \frac{I}{I_0}$$

Absorbance is defined by

$$A \equiv \ell\log_{10}\left(\frac{I_0}{I}\right) \qquad (33)$$

There are both advantages and limitations to the use of either T or A. Transmittance values are contained within the interval from zero to unity, whereas absorbance values can range from zero to infinity.

Transmittance is related to concentration in an awkward way, but absorbance is a convenient linear function of concentration.

A derivation and discussion of the Bouger-Beer law is given in M. G. Mellon, Analytical Absorption Spectroscopy, New York: John Wiley & Sons, Inc., 1950, pp. 90-101. This book remains an excellent source of information about spectrophotometry, although continuing rapid advances in instrumentation make it necessary to supplement such a book with the latest information from instrument manufacturers. Alternative derivations of the Bouger-Beer Law are given by H. A. Liebhafskey and H. G. Pfeiffer, J. Chem. Educ., 30, 450 (1953), and by J. H. Goldstein and R. A. Day, J. Chem. Educ., 31, 417 (1954).

We shall now investigate how this linear dependence of A on concentration comes about. Equations 30 and 33 are combined, taking advantage of two fundamental properties of logarithms:

$$\log_{10} 10^{x} = x$$

$$10^{-x} = \frac{1}{10^{x}}$$

The result is

$$A = \ell\varepsilon_{X}(X) \qquad (34)$$

for a solution containing the single absorbing species X. The corresponding equation relating absorbance to concentrations for a solution with two absorbing chemical species is obtained by combining Equations 31 and 33. The result is

$$A = \ell\varepsilon_{X_1}(X_1) + \ell\varepsilon_{X_2}(X_2) \qquad (35)$$

An important chemical research tool is the optical absorption spectrophotometer, an instrument used to measure the amount of monochromatic light absorbed by a sample. White light comes from an incandescent tungsten-filament electric light bulb for measurements in the visible portion of the spectrum, and this light is passed through a prism or grating monochromator. Monochromatic light comes from the monochromator as a narrow band of wavelengths

distributed around a nominal value shown on the monochromator dial. Numerical values of absorbance are obtained by determining, with a photosensitive detector, the intensity of a light beam that passes through a transparent cell containing the solution.

If, at the wavelength chosen, the only significant light absorption is due to the two indicator species HI and I^-, then the absorbance of the solution is given by

$$A = \ell\varepsilon_{HI}(HI) + \ell\varepsilon_{I^-}(I^-) \qquad (36)$$

where ε_{HI} and ε_{I^-} are the molar absorptivities of species HI and I^-. We can conveniently measure A in the laboratory, but there is no direct method of measuring (HI) or (I^-), so we seek now to eliminate both (HI) and (I^-) from Equation 36. We seek an equation relating only experimentally-measurable variables. Combination of Equations 20 and 23 gives both

$$[I] = (HI)\left(1 + \frac{K_{HI}}{(H^+)}\right) \qquad (37)$$

$$[I] = (I^-)\left(\frac{(H^+)}{K_{HI}} + 1\right) \qquad (38)$$

Then introduction of both Equations 37 and 38 into Equation 36 gives

$$A = [I]\ell\left(\frac{\varepsilon_{HI}}{1 + \frac{K_{HI}}{(H^+)}} + \frac{\varepsilon_{I^-}}{\frac{(H^+)}{K_{HI}} + 1}\right) \qquad (39)$$

Rearranging, we get

$$A = [I]\ell\left(\frac{\varepsilon_{HI}(H^+)}{(H^+) + K_{HI}} + \frac{\varepsilon_I - K_{HI}}{(H^+) + K_{HI}}\right)$$

$$= \frac{[I]\ell}{(H^+) + K_{HI}}\left(\varepsilon_{HI}(H^+) + \varepsilon_I - K_{HI}\right) \qquad (40)$$

Introduction of volume variables by means of Equations 25, 26, and 27 transforms Equation 40 into

$$A = \left(\frac{V_{HI}M_{HI}}{V_{HI} + V_{HA} + V_{NaOH}}\right)\left(\frac{\ell}{(H^+) + K_{HI}}\right)\left(\varepsilon_{HI}(H^+) + \varepsilon_I - K_{HI}\right) \qquad (41)$$

If, at some particular point in the titration, paired values of (H^+) and V_{NaOH} are known, then Equation 41 can be used to calculate the value of A at that point. Our computer calculation of A versus V_{NaOH} will use this procedure. Equations 29 and 41 will be used together for the calculations.

Computer calculations could give us insight into several questions about the use and usefulness of indicators in the titration of an acid with a base:

- *By how much do the values of the two absorptivities have to differ in order that a sharp absorbance change can occur?*
- *What are the restrictions on the value of K_{HI} consistent with an abrupt absorbance change?*
- *Does an abrupt absorbance change necessarily coincide with the equivalence point?*
- *Is it possible to have an abrupt change in absorbance without a correspondingly abrupt change in (H^+)?*
- *Can an absorbance change occur before the equivalence point? after the equivalence point?*

FORTRAN COMPUTER PROGRAM

FORTRAN Program 7 begins with a trial value of (H^+), and calculates a value of V_{NaOH}, using Equation 29. If the calculated value of V_{NaOH} is negative, a smaller value of (H^+) is chosen, and the calculation is made again. This procedure continues until a positive volume is obtained, and then that value of (H^+) is also used to calculate the value of A by using Equation 41. A graph of A versus V_{NaOH} is drawn from the points obtained from the series of further calculations, each calculation made from a smaller value of (H^+). Finally (H^+) becomes so small that the calculated volume of titrant again becomes negative, and then this phase of the program is completed. Then on the same coordinates, a plot of pH versus V_{NaOH} is drawn with numbers obtained from a new set of calculations. The statement following statement 22 adjusts the scale axes so that pH, ranging from 4 to 13, can be plotted on the same axes as absorbance, ranging from 0 to 1. The quantities B, C, D, E, and F were introduced for convenience in punching cards, on the assumption that the chance of errors in punching was thereby reduced.

CONCLUSIONS: SOME GENERALIZATIONS ABOUT THE PRACTICAL USE OF AN INDICATOR

The results of some representative calculations are presented on the following pages. It is clear that an abrupt change in color of the solution (an abrupt increase in the absorbance for the cases presented here) can be achieved if K_{HI} has a numerical value equal to a value of (H^+) within a nearly-vertical portion of the pH-volume curve near the equivalence point. The sharpest endpoint is found when K_{HI} has a value equal

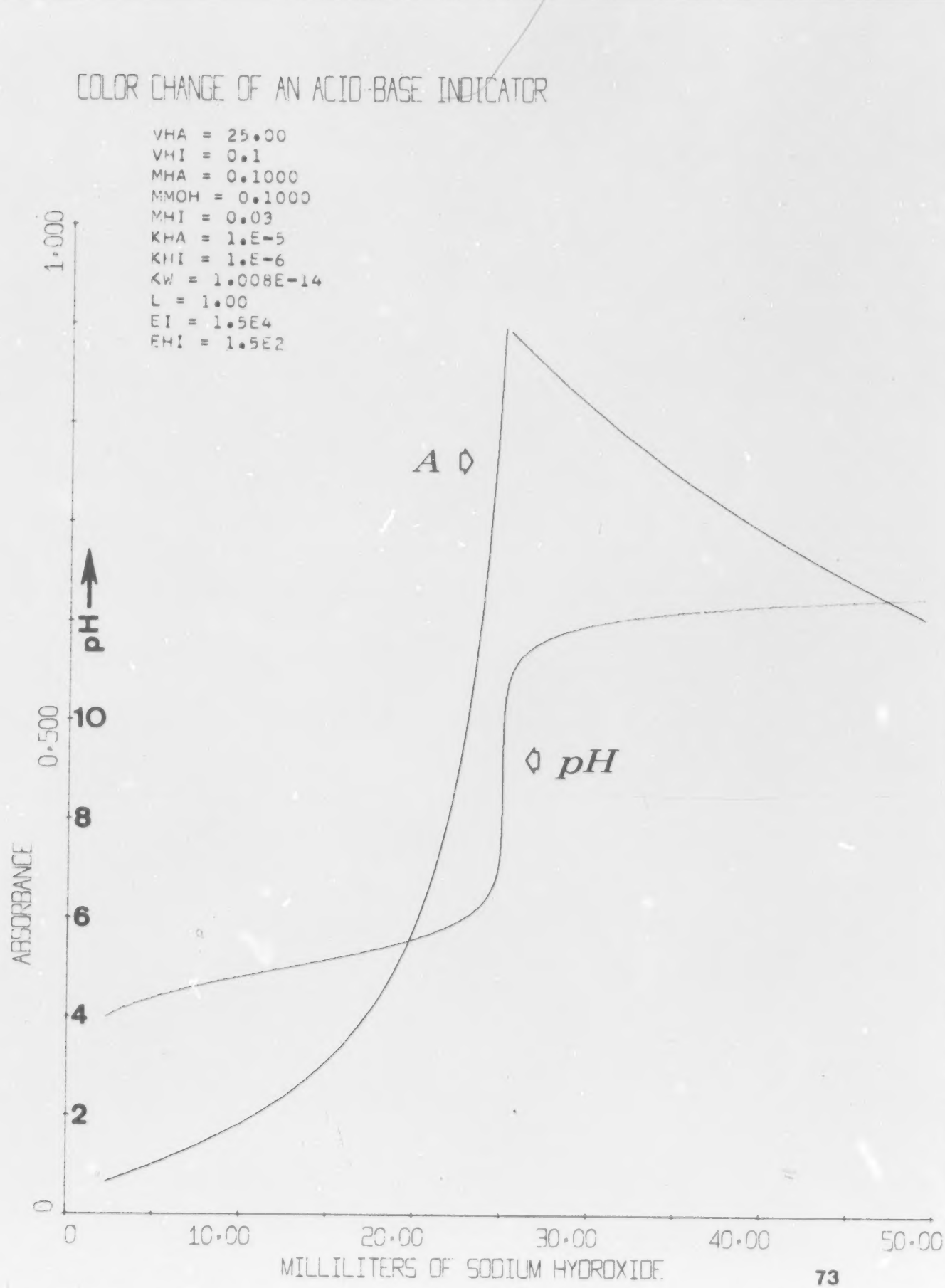
7

```
// JOB                    S71007,S51


// FOR
* LIST SOURCE PROGRAM
*ONE WORD INTEGERS
*IOCS(CARD, 1132 PRINTER, TYPEWRITER, PLOTTER)
C       COLOR CHANGE OF AN INDICATOR
        REAL KHA, KW, KHI, MHA, MMOH, MHI, L
        VHA = 25.00
        VHI = 0.1
        MHA = 0.1000
        MMOH = 0.1000
        MHI = 0.03
        KHA = 1.E-5
        KHI = 1.E-12
        KW = 1.008E-14
        L = 1.00
        EI = 1.5E4
        EHI = 1.5E2
        CALL PREP (.14, 8., 1., 1.)
        WRITE (7,15)
   15 FORMAT ('COLOR CHANGE OF AN ACID-BASE INDICATOR')
        CALL YAXIS (0., 0., .1, 10, 2)
        WRITE (7,17)
   17 FORMAT ('ABSORBANCE                .05PH')
        CALL XAXIS (0., 0., 5., 10, 5)
        WRITE (7,16)
   16 FORMAT ('MILLILITERS OF SODIUM HYDROXIDE')
        H = 1.
    1   H = .1*H
        E = VHA*(H**3 + KHA*(H**2) - (KHA*MHA + KW)*H - KW*KHA)
        F = VHI*(H**3 + KHA*(H**2) - KW*H - KW*KHA)
        DEN =  H**3 + (KHA + MMOH)*(H**2) + (KHA*MMOH - KW)*H - KW*KHA
        VMOH = -(E + F)/DEN
        B = VHI*MHI/(VHI + VMOH + VHA)
        C = L/(H + KHI)
        D = EHI*H + EI*KHI
        A = B*C*D
        IF (VMOH) 1,2,2
    2   CALL FPLOT (-2,VMOH,A)
    5   H = H - .1*H
        E = VHA*(H**3 + KHA*(H**2) - (KHA*MHA + KW)*H - KW*KHA)
        F = VHI*(H**3 + KHA*(H**2) - KW*H - KW*KHA)
        DEN =  H**3 + (KHA + MMOH)*(H**2) + (KHA*MMOH - KW)*H - KW*KHA
        VMOH = -(E + F)/DEN
        B = VHI*MHI/(VHI + VMOH + VHA)
        C = L/(H + KHI)
        D = EHI*H + EI*KHI
        A = B*C*D
        IF(50.-VMOH) 10,3,3
    3   CALL FPLOT (0,VMOH,A)
        GO TO 5
   10   CONTINUE
        CALL FPLOT (1,VMOH,A)
```

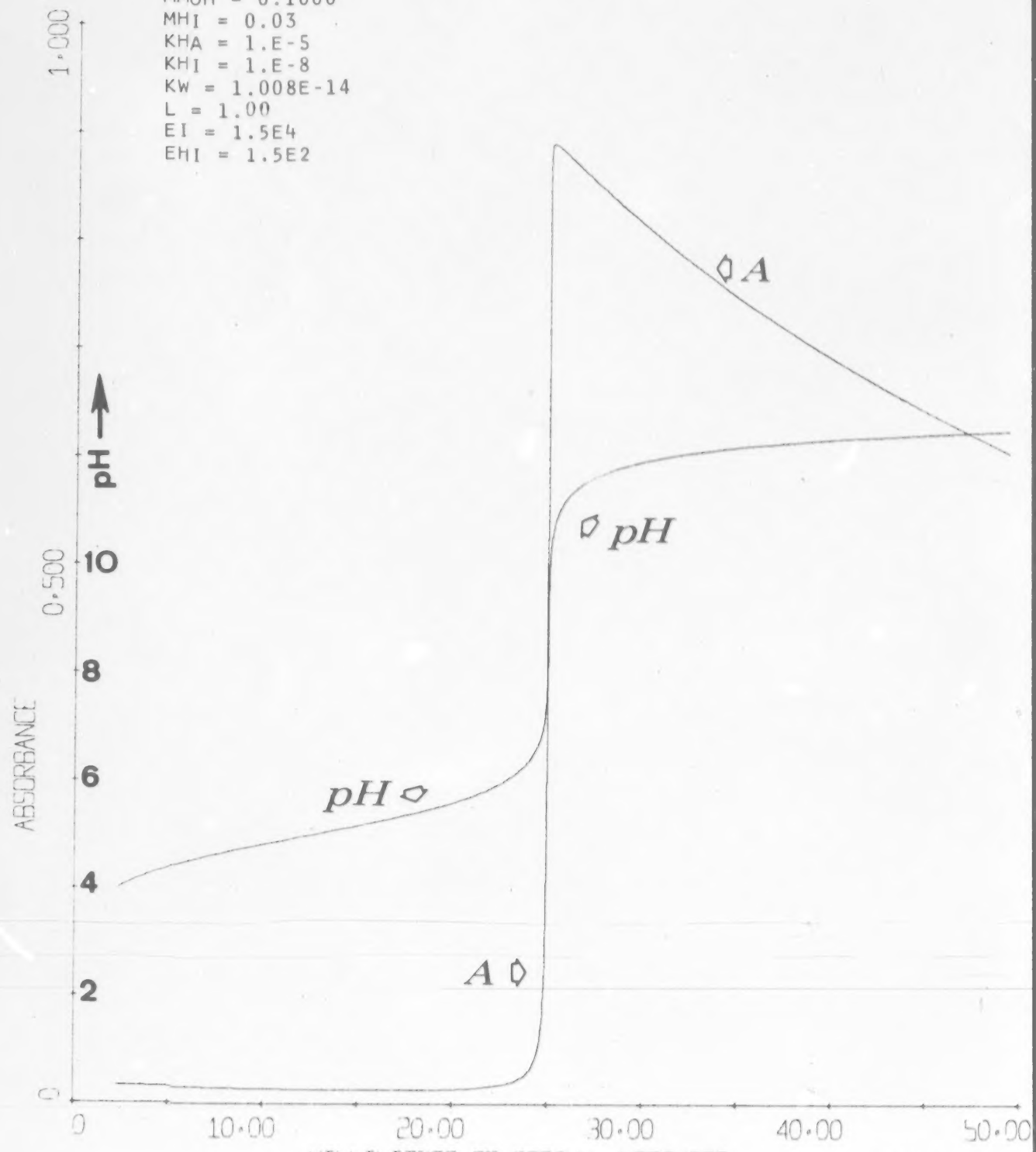
```
      H = 1.
   21 H = .1*H
      E = VHA*(H**3 + KHA*(H**2) - (KHA*MHA + KW)*H - KW*KHA)
      F = VHI*(H**3 + KHA*(H**2) - KW*H - KW*KHA)
      DEN =  H**3 + (KHA + MMOH)*(H**2) + (KHA*MMOH - KW)*H - KW*KHA
      VMOH = -(E + F)/DEN
      IF (VMOH) 21,22,22
   22 PH = -(ALOG(H))/2.303
      P = PH/20.
      CALL FPLOT (-2,VMOH,P)
   25 H = H - .1*H
      E = VHA*(H**3 + KHA*(H**2) - (KHA*MHA + KW)*H - KW*KHA)
      F = VHI*(H**3 + KHA*(H**2) - KW*H - KW*KHA)
      DEN =  H**3 + (KHA + MMOH)*(H**2) + (KHA*MMOH - KW)*H - KW*KHA
      VMOH = -(E + F)/DEN
      PH = -(ALOG(H))/2.303
      P = PH/20.
      IF(50.-VMOH) 30,23,23
   23 CALL FPLOT (0,VMOH,P)
      GO TO 25
   30 CALL FINPL
      CALL EXIT
      END
```

```
// XEQ
```


COLOR CHANGE OF AN ACID-BASE INDICATOR
VHA = 25.00
VHI = 0.1
MHA = 0.1000
MMOH = 0.1000
MHI = 0.03
KHA = 1.E-5
KHI = 1.E-6
KW = 1.008E-14
L = 1.00
EI = 1.5E4
EHI = 1.5E2
1.000
0.500
0
ABSORBANCE
pH
10
8
6
4
2
A
pH
0
10.00
20.00
30.00
40.00
50.00
MILLILITERS OF SODIUM HYDROXIDE

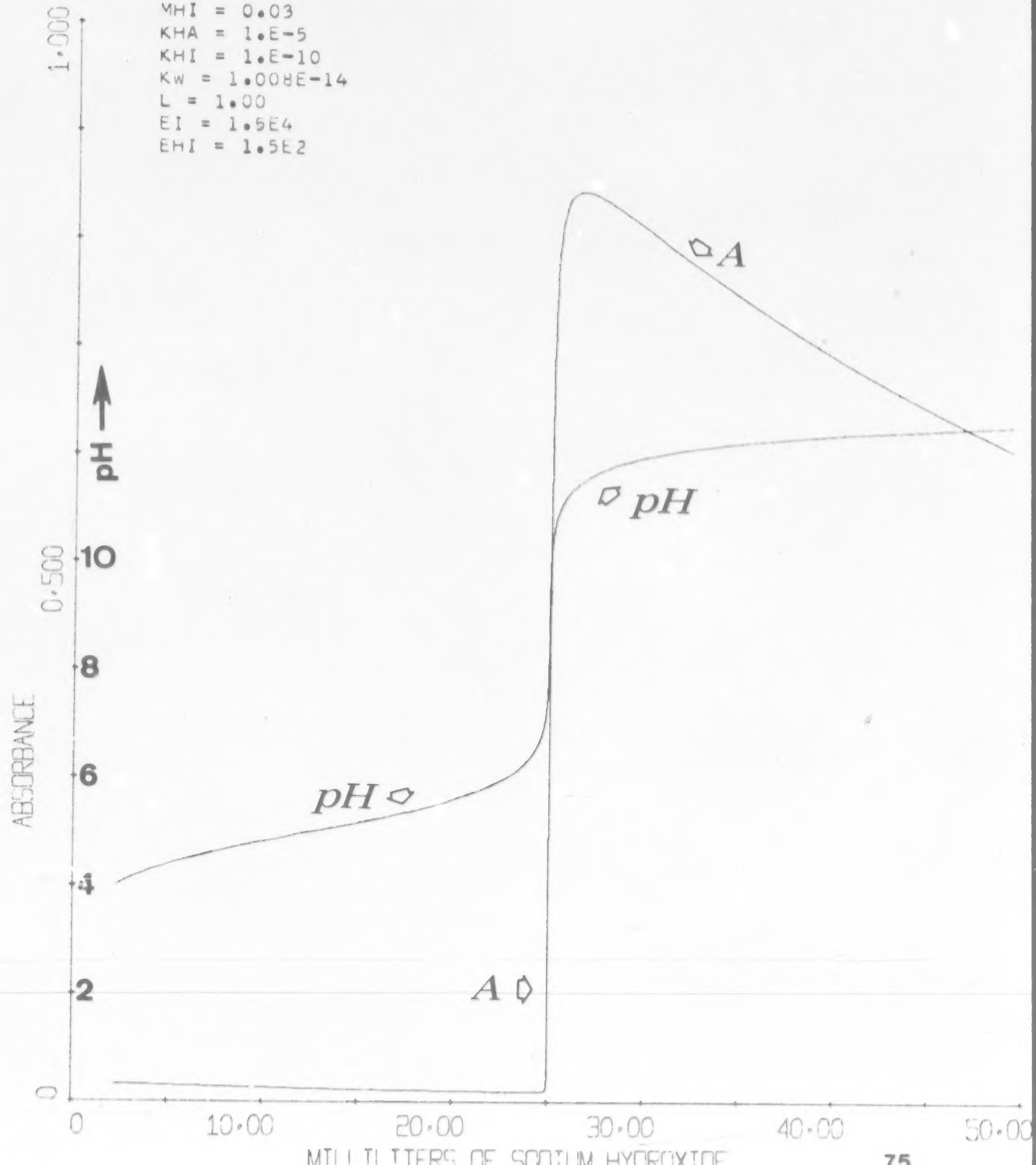
COLOR CHANGE OF AN ACID-BASE INDICATOR

VHA = 25.00
VHI = 0.1
MHA = 0.1000
MMOH = 0.1000
MHI = 0.03
KHA = 1.E-5
KHI = 1.E-8
KW = 1.008E-14
L = 1.00
EI = 1.5E4
EHI = 1.5E2



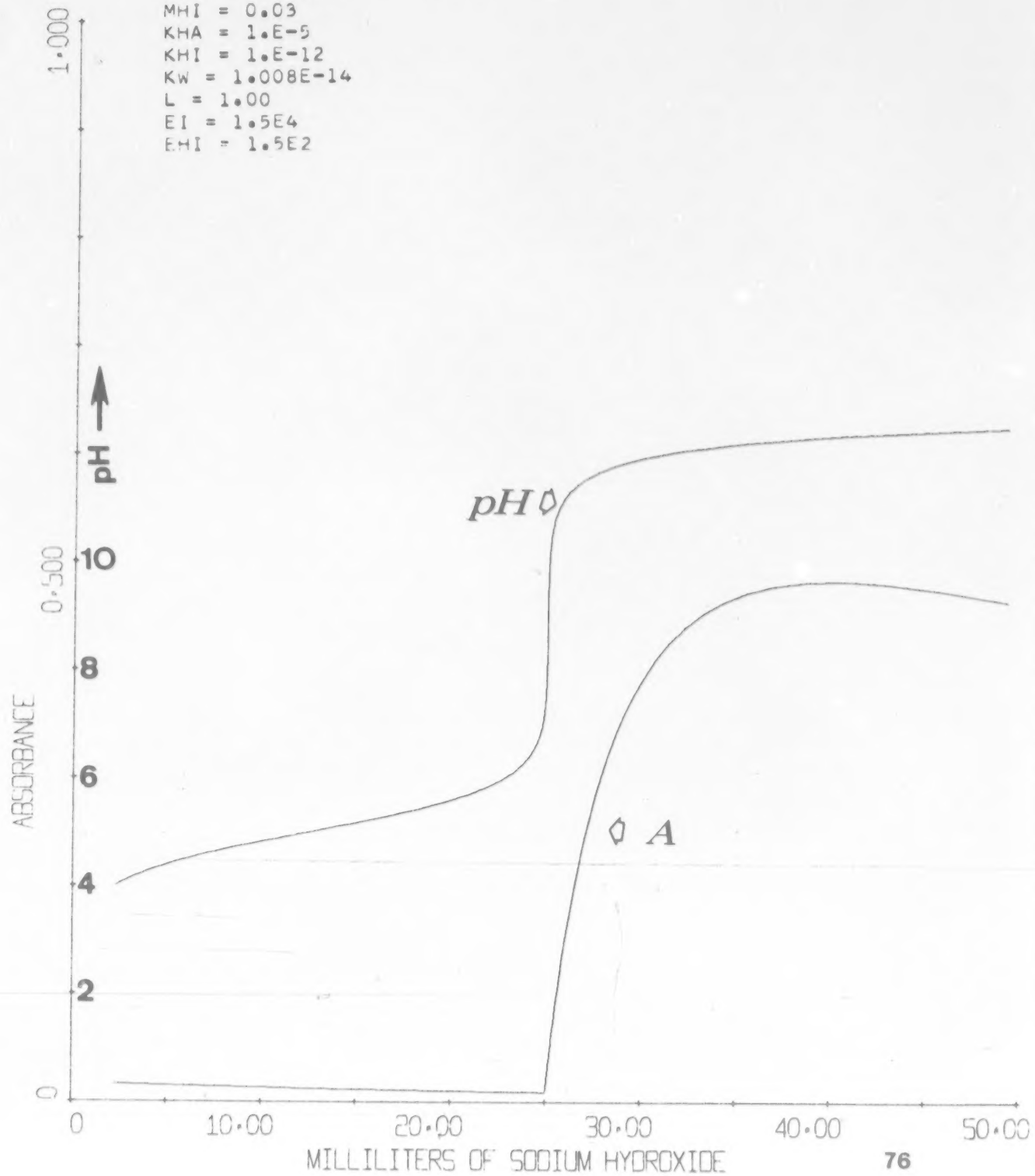
COLOR CHANGE OF AN ACID-BASE INDICATOR

VHA = 25.00
VHI = 0.1
MHA = 0.1000
MMOH = 0.1000
MHI = 0.03
KHA = 1.E-5
KHI = 1.E-10
Kw = 1.008E-14
L = 1.00
EI = 1.5E4
EHI = 1.5E2



COLOR CHANGE OF AN ACID-BASE INDICATOR

VHA = 25.00
VHI = 0.1
MHA = 0.1000
MMOH = 0.1000
MHI = 0.03
KHA = 1.E-5
KHI = 1.E-12
KW = 1.008E-14
L = 1.00
EI = 1.5E4
EHI = 1.5E2



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to (H^+) at the basic side of this equivalence zone.

If the indicator has an equilibrium constant 100 times too large or too small, then no abrupt change of color will be observed, and the color change that does occur may not take place at the equivalence point.

These calculations assumed a particular set of values of K_{HA}, M_{HA}, and M_{NaOH}. A different acid, and a different set of concentrations, would be expected to affect the results. What does your chemical intuition say? How can you check your intuition?

CHANGES IN THE TWO DISTRIBUTION FRACTIONS DURING THE TITRATION OF A MONOPROTIC ACID

A fruitful way of thinking about the shifts in chemical equilibria that occur continuously during a titration is to look at the behavior of the *species distribution fractions* during that titration. The species distribution fractions are functions that tell quantitatively, for each value of (H^+), how the protons are distributed between HA and A^-, and how total A is distributed between these two chemical species. For the case of the monoprotic acid HA being titrated with NaOH, the two fractions are

$$\frac{(HA)}{[A]} \quad \text{and} \quad \frac{(A^-)}{[A]}$$

Note that $(HA)/[A]$ is the fraction of all A-containing species present in solution as HA, and that $(A^-)/[A]$ is the fraction present as A^-. To obtain algebraic equations relating these fractions to (H^+), we shall combine the defining eq ation for the equilibrium constant K_{HA} with the conservation equation for all A-containing species. Thus, Equations 8 and 10 can be readily combined to give

$$[A] = (HA)\left(1 + \frac{K_{HA}}{(H^+)}\right)$$

whereupon rearrangement yields

$$\frac{(HA)}{[A]} = \frac{1}{1 + \dfrac{K_{HA}}{(H^+)}} = \frac{(H^+)}{(H^+) + K_{HA}} \qquad (42)$$

In the same manner, we can again start with Equations 8 and 10, this time obtaining

$$[A] = (A^-)\left[1 + \frac{(H^+)}{K_{HA}}\right]$$

which can be rearranged to give

$$\frac{(A^-)}{[A]} = \frac{1}{1 + \dfrac{(H^+)}{K_{HA}}} = \frac{K_{HA}}{(H^+) + K_{HA}} \qquad (43)$$

- *Show that the sum of the two distribution fractions is equal to 1.*
- *Show that when* (H^+) *is substantially greater than* K_{HA}, *the predominant species in solution is* HA.
- *Show that when* (H^+) *is much less than* K_{HA}, A^- *is the predominant species.*
- *When the two distribution fractions equal one another (and thus each is equal to* $\frac{1}{2}$*), what is the numerical value of* (H^+)*?*

To illustrate the use of distribution fractions, let us investigate the chemical changes involved during the titration of a monoprotic acid with a dissociation constant equal to 10^{-5} (that is, with $pK_{HA} = 5$). FORTRAN Program 8 can be used to plot the titration curve and the two distribution fractions (see the output on pages 85 to 88). The fraction (HA)/[A] is almost equal to 1.0 at the beginning of the titration, meaning that in this 0.1 molar solution of acid in water, most of the acid is undissociated. Then during the titration, the fraction decreases essentially linearly with addition of NaOH, reaching the value 0.0 almost exactly at the equivalence point. The fraction $(A^-)/[A]$ begins almost at zero, and increases linearly to 1.0 at the equivalence

point. From the beginning of the titration to the equivalence point, each aliquot of sodium hydroxide solution has the same incremental effect on each of the fractions.

Then, at the equivalence point, the situation markedly changes. Further addition of titrant has no observable effect on either fraction. There is a qualitative change in the dependence of the fractions on volume of added titrant. Each fraction ceases its linear change, and remains essentially equal to either zero or to one.

> The fraction (HA)/[A] reaches essentially zero on the <u>linear</u> scale; on a logarithmic scale, we would observe this function to continue its decrease. In fact, for $(H^+) \ll K_{HA}$, Equation 42 assumes the limiting form $(HA)/[A] \simeq (H^+)/K_{HA}$, and the value of the fraction plunges toward zero together with the value of (H^+).

This qualitative change signals a change in the whole character of the significant equilibria; the chemistry is different. The entire first portion of the titration from start to equivalence point can be described accurately as the reaction of NaOH with HA. However, at the equivalence point the solution is unable to furnish unreacted HA to continue the reaction. The equivalence point in this titration marks a sharp dividing line between two very different chemical situations. The most dramatic occurrence seen on these plots is at the equivalence point on the plot of pH versus V_{NaOH}, where the quantity (H^+) changes by a factor of a million with the addition of just a few milliliters of titrant; this change is abrupt even on the logarithmic pH scale. It is this abrupt change that permits the reliable detection of the

equivalence point in the titration.

Note that both distribution fractions are equal to ½ at the macroscopic half-equivalence point, and that the pH at that point is numerically equal to the value of pK_{HA}.

For a substantially stronger acid, the picture drawn by the distribution-fraction curves is different in several significant respects. A stronger acid (see the curves on pages 85 and 86) is dissociated to a greater degree at the beginning of the titration. With an acid having $pK_{HA} = 5$, we could say with justification that equimolar amounts of OH^- (from the NaOH solution) and HA react following each addition of titrant prior to the equivalence point. With the stronger acids (acids with a larger value of K_{HA}, and a smaller value of pK_{HA}), the slope of the (HA)/[A] versus V_{NaOH} curve is less steep, and this fact can be interpreted as meaning that OH^- from the titrant reacts only partly with HA and also partly with H^+.

With very weak acids, the distribution fractions do not change linearly during the titration (see page 88), noticeably just before the equivalence point. Some HA remains in solution even after the equivalence point has been passed. Endpoint detection is then difficult and less precise, primarily because there is no longer a qualitative difference between the chemistry just before and just after the equivalence point. Note that this plot suggests a requirement for an abrupt pH change at the equivalence point: *the slope of the distribution-fraction curve, plotted on a linear scale versus volume of added titrant, must change abruptly at the equivalence point.*

The arguments of the preceding section are based on graphs in which (H^+) is presented logarithmically, and each of the distribution fractions is presented linearly. You may wish to consider whether such presentations are appropriate for a faithful and informative presentation of the relevant facts. It is possible that this presentation distorts some relationships. Feel free to make your own computer-drawn graphs, plotted in other ways, and to draw your own conclusions about the chemistry.

COMPUTER CALCULATION OF THE DISTRIBUTION FRACTIONS FOR A MONOPROTIC ACID

Calculation of the fractions $(A^-)/[A]$ and $(HA)/[A]$ as functions of V_{NaOH} proceeds by considering the concentration (H^+) to be a master variable that connects Equations 16, 42, and 43. The chemical reason for this algebraic convenience is that the chemical spevies H^+ is common to the two chemical equilibria, providing a chemical coupling between the two reactions in solution. For a particular value of (H^+), use of Equation 16 yields the paired value of V_{NaOH}, Equation 42 gives $(HA)/[A]$, and Equation 43 gives $(A^-)/[A]$.

This program introduces two new FORTRAN features: writing and use of a stored subroutine, and storage of variables in COMMON. The COMMON statement has the general form

```
COMMON A, B, C, ...
```

where A, B, C, ... are variable names. Five variables are assigned to COMMON by our main program, and the values of these variables are available for use by the subroutine without being redefined in the subroutine.

The subroutine appears first, so that it can be used later

8

```
// JOB                  S71007,S51


// FOR
* LIST SOURCE PROGRAM
*IOCS(CARD, 1132 PRINTER, TYPEWRITER, PLOTTER)
*ONE WORD INTEGERS
      REAL NUM, KHA, MMOH, KW, MHA
      COMMON V,HH,KHA,MMOH,KW,MHA,VHA
C     SUBROUTINE PLOT2
C     CALCULATION AND PLOTTING OF THE DISTRIBUTION FRACTIONS
      CALL PREP (.14, 4., 1., 1.)
      CALL YAXIS (0., 0., .1, 10, 2)
      WRITE (7,37)
   37 FORMAT ('DISTRIBUTION FRACTION')
      CALL XAXIS (0., 0., 1., 50, 10)
      WRITE (7,56)
   56 FORMAT ('MILLILITERS OF SODIUM HYDROXIDE')
      VMOH = V
      H = HH
      FHA = H/(H + KHA)
      CALL FPLOT (-2,VMOH,FHA)
   35 H = H - .1*H
      DEN =  H**3 + (KHA + MMOH)*(H**2) + (KHA*MMOH - KW)*H - KW*KHA
      NUM = H**3 + KHA*(H**2) - (KW + (KHA*MHA))*H - KW*KHA
      VMOH = -VHA*NUM/DEN
      FHA = H/(H + KHA)
      IF(50.-VMOH) 30,33,33
   33 CALL FPLOT (0,VMOH,FHA)
      GO TO 35
   30 VMOH = V
      H = HH
      FA = KHA/(H + KHA)
      CALL FPLOT (1,VMOH,FA)
      CALL FPLOT (-2,VMOH,FA)
   45 H = H - .1*H
      DEN =  H**3 + (KHA + MMOH)*(H**2) + (KHA*MMOH - KW)*H - KW*KHA
      NUM = H**3 + KHA*(H**2) - (KW + (KHA*MHA))*H - KW*KHA
      VMOH = -VHA*NUM/DEN
      FA = KHA/(H + KHA)
      IF (50.-VMOH) 40,43,43
   43 CALL FPLOT (0,VMOH,FA)
      GO TO 45
   40 CALL FINPL
      CALL EXIT
      END

// DUP

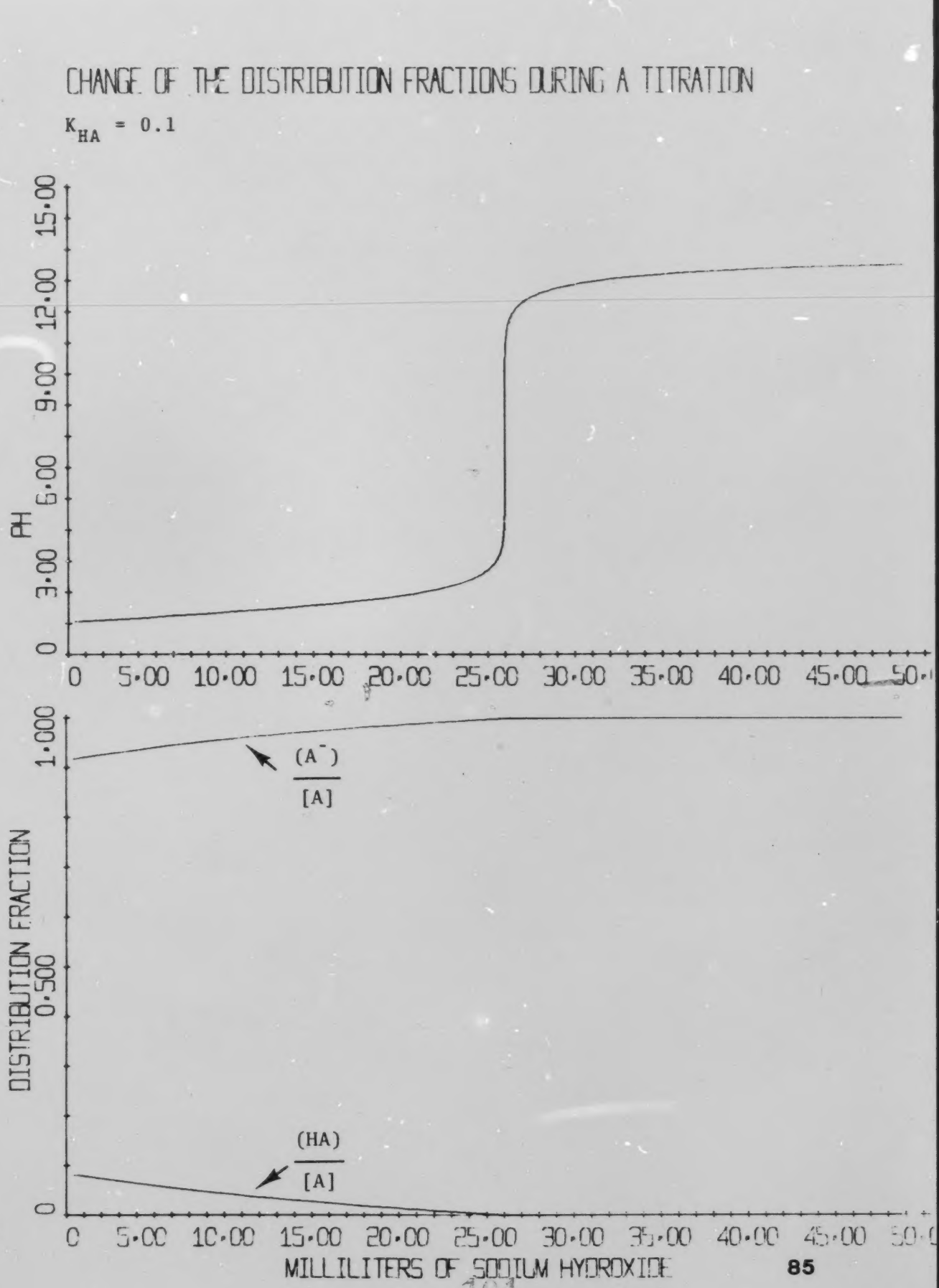
*STORE       WS  UA  PLOT2
```

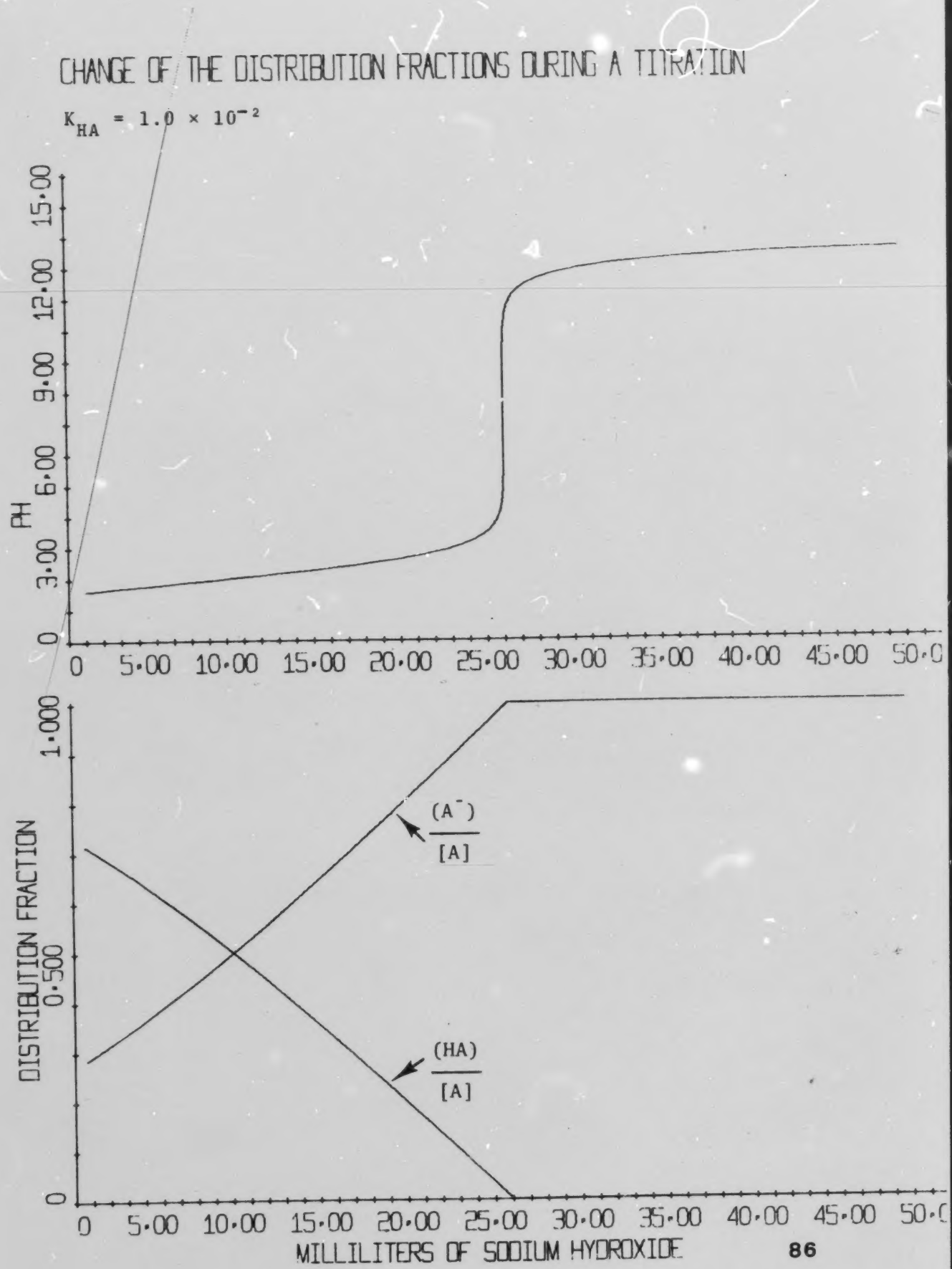
```
// FOR
*IOCS(CARD, 1132 PRINTER, TYPEWRITER, PLOTTER)
* LIST SOURCE PROGRAM
*ONE WORD INTEGERS
      REAL KHA, KW, NUM, MHA, MMOH
      COMMON V,HH,KHA,MMOH,KW,MHA,VHA
C     CHANGES IN THE TWO DISTRIBUTION FRACTIONS DURING A TITRATION
      VHA = 25.00
      MHA = 0.1000
      MMOH = 0.1000
      KHA = 1.E-10
      KW = 1.008E-14
      CALL PREP (.14, .25, 1., 5,5)
      WRITE (7,15)
   15 FORMAT ('CHANGE OF THE DISTRIBUTION FRACTIONS DURING A TITRATION')
      CALL YAXIS (0.,0.,1.,15,5)
      WRITE (7,17)
   17 FORMAT ('PH')
      CALL XAXIS (0.,0.,1.,50,10)

C     CALCULATION OF THE FIRST POINT OF THE TITRATION CURVE
      H = 1.
    1 H = H - .1*H
      PH = -(ALOG(H))/2.303
      NUM = H**3 + KHA*(H**2) - (KW + (KHA*MHA))*H - KW*KHA
      DEN =  H**3 + (KHA + MMOH)*(H**2) + (KHA*MMOH - KW)*H - KW*KHA
      VMOH = -VHA*NUM/DEN
      IF (VMOH) 1,2,2
    2 CALL FPLOT (-2,VMOH,PH)
      V = VMOH

C     CALCULATION AND PLOTTING OF THE TITRATION CURVE
      HH = H
    5 H = H - .1*H
      PH = -(ALOG(H))/2.303
      DEN =  H**3 + (KHA + MMOH)*(H**2) + (KHA*MMOH - KW)*H - KW*KHA
      NUM = H**3 + KHA*(H**2) - (KW + (KHA*MHA))*H - KW*KHA
      VMOH = -VHA*NUM/DEN
      IF(50.-VMOH) 10,3,3
    3 CALL FPLOT (0,VMOH,PH)
      GO TO 5
   10 CALL FINPL
      CALL LINK(PLOT2)
      END

// XEQ
```


CHANGE OF THE DISTRIBUTION FRACTIONS DURING A TITRATION
K_{HA} = 0.1
PH
0
3·00
6·00
9·00
12·00
15·00
0
5·00
10·00
15·00
20·00
25·00
30·00
35·00
40·00
45·00
DISTRIBUTION FRACTION
0
0·500
1·000
(A⁻)
[A]
(HA)
[A]
MILLILITERS OF SODIUM HYDROXIDE


CHANGE OF THE DISTRIBUTION FRACTIONS DURING A TITRATION
$K_{HA} = 1.0 \times 10^{-2}$
PH
0
3·00
6·00
9·00
12·00
15·00
0
5·00
10·00
15·00
20·00
25·00
30·00
35·00
40·00
45·00
50·0
DISTRIBUTION FRACTION
0
0·500
1·000
$\frac{(A^-)}{[A]}$
$\frac{(HA)}{[A]}$
0
5·00
10·00
15·00
20·00
25·00
30·00
35·00
40·00
45·00
50·0
MILLILITERS OF SODIUM HYDROXIDE

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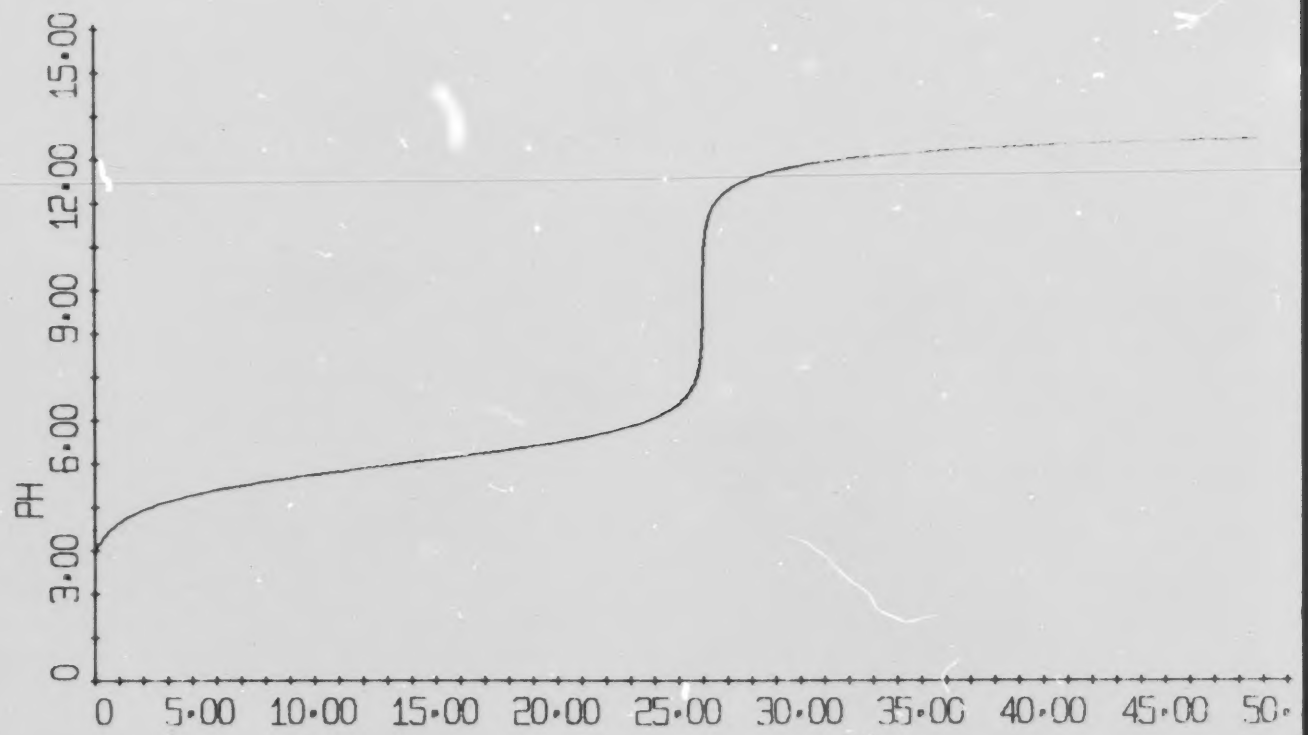
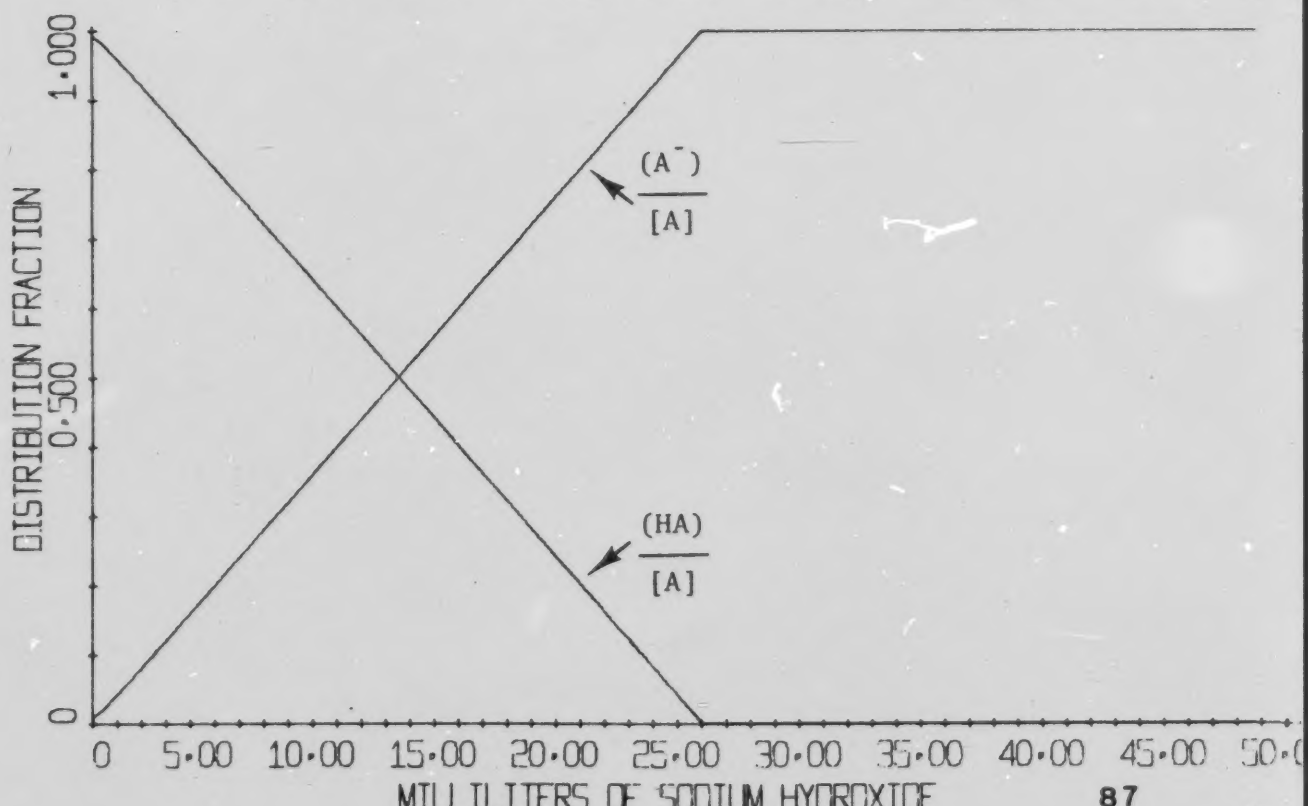
CHANGE OF THE DISTRIBUTION FRACTIONS DURING A TITRATION

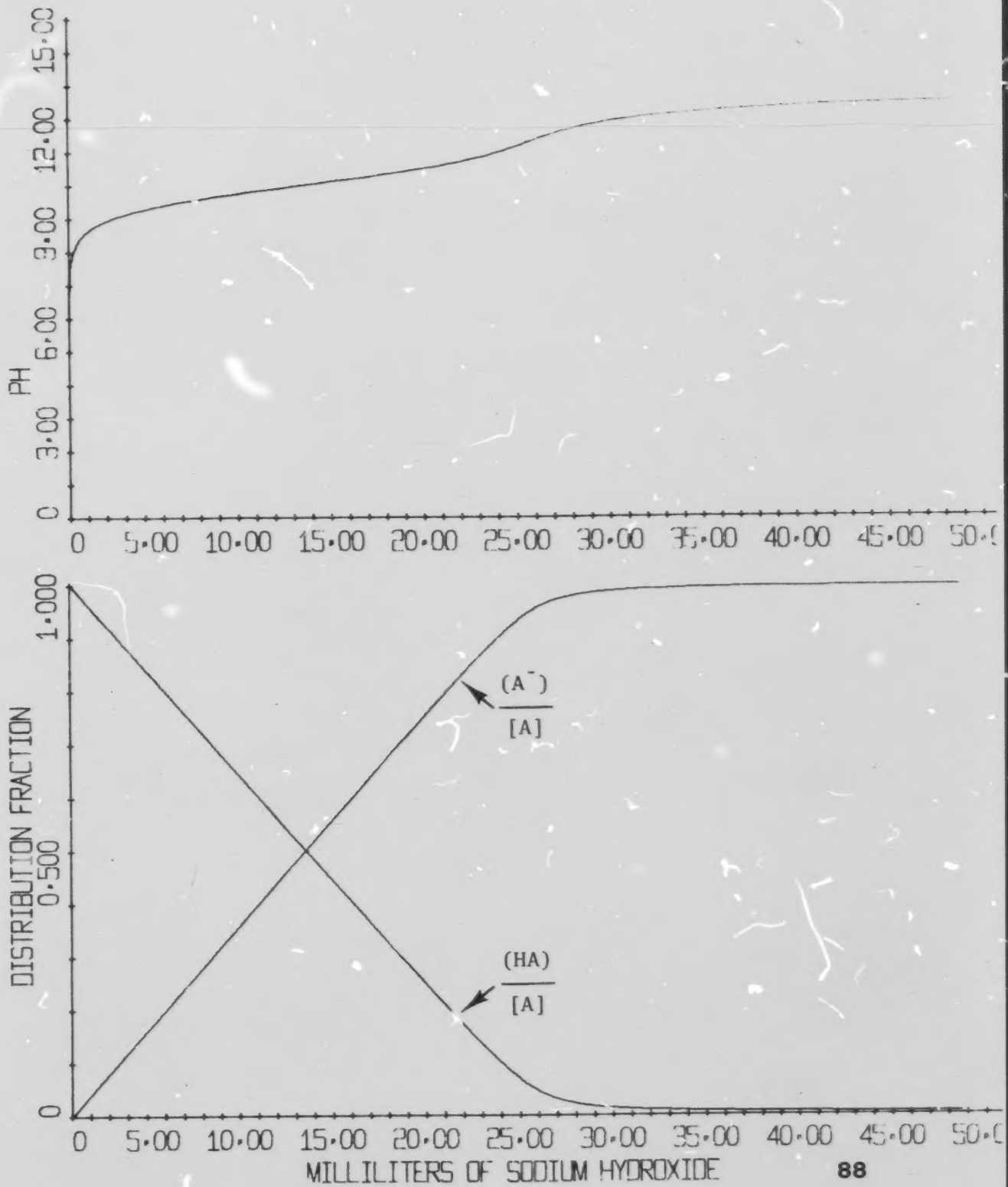
$K_{HA} = 1.0 \times 10^{-5}$





CHANGE OF THE DISTRIBUTION FRACTIONS DURING A TITRATION

$K_{HA} = 1.0 \times 10^{-10}$



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when needed in the main program. The subroutine is written as an ordinary program, with a specification of the variables the subroutine expects to find in COMMON. The last statement is END. The programmer decides on some name for the subroutine, and then uses the // DUP statement and the *STORE statement to transfer the subroutine into a temporary storage location on the disk.

We then proceed to the main program, written in the usual manner. The COMMON statement instructs the computer to store in COMMON each of the five variables whenever they are defined, and to replace these values with new values whenever the variables are redefined.

The CALL LINK statement calls the subroutine from disk storage into the working core memory, and transfers control to the first statement of the subroutine. The general form of the statement is

```
CALL LINK (NAME)
```

where NAME is the name of a subroutine already stored on the disk.

There are two distinct plotting programs, and in each case there is a pause in the execution before the plotter begins plotting to allow you to set the pen in the proper location on the paper. Careful readjustment of the pen position is necessary to assure that the second plot will be located on the paper directly under the first.

COMPUTER CALCULATIONS USING THE BASIC PROGRAMMING LANGUAGE AND A TIME-SHARING TERMINAL

Many of the computer calculations illustrated by FORTRAN programs can be readily performed using a remote terminal for input and output. There are some advantages, as well as some limitations, to use of a simple teletype or teletypewriter terminal. The principal advantage is the ease with which the user can interact with the program. Disadvantages of the simplest terminals include the necessity of relying on keyboard input of programs and data (punched cards, while more difficult to prepare, are more reliable for repeat runs), and the lack of high-resolution plotting capability. In essence, batch processing of cards with an IBM 1130 system that includes a high-resolution plotter is *different* than time-sharing computations from a simple terminal. Some illustrative programs, all written in BASIC programming language, are presented on the following pages to show how the inherent advantages of a terminal may be utilized for learning more about the chemistry of monoprotic carboxylic acids.

BASIC Program A is written to provide simulated data from a titration of the acid HA with a solution of NaOH. The variables are given short names (for example, A, B, C, ...) so that the program can be typed with a minimum of effort. The output is printed as a listing of paired values of V_{NaOH} and pH.

Let us examine this program in detail. The program is based on Equation 16, and this equation appears in a somewhat disguised form in statements 100, 110, and 120. Rather than use the symbols

Table 2

ARITHMETIC SYMBOLS USED IN THE BASIC PROGRAMMING LANGUAGE

+	addition sign
-	subtraction sign
/	division sign
*	multiplication sign (do not indicate multiplication with just parentheses)
↑	means raised to the power of
=	equals sign

RELATIONAL SYMBOLS

<	less than
<=	less than or equal to
=	equal to
>	greater than
>=	greater than or equal to
<>	not equal to

directly from Equation 16, we have used certain arithmetic symbols from the listing in Table 2, and we have given the various variables the following short names:

Code for Translating Program into Algebra

BASIC Symbol	Algebraic Symbol
A	K_{HA}
B	V_{HA}
C	M_{HA}
D	M_{NaOH}
E	K_w
I	change in (H^+)
H	(H^+)
P	pH
N	*numerator*
D1	*denominator*
V	V_{NaOH}

Large and small numbers are written in *exponential notation*, which means that two of the BASIC statements translate as follows:

A=1.75E-5 ⇒ $K_{HA} = 1.75 \times 10^{-5}$

E=1.01E-14 ⇒ $K_w = 1.01 \times 10^{-14}$

Each typewritten line in the program is called a *statement*, and each statement has a number. The first statements define various variables and constants, and state the initial conditions of the titration. Unless there are instructions to the contrary, the computer proceeds sequentially through the statements in numerical order according to their statement numbers. After one

A

```
10 A=1.75E-5
20 B=25
30 C=.1
40 D=.1
50 E=1.01E-14
60 I=.5
70 H=1
80 H=H*I
90 P=-(LOG(H))/2.303
100 N=H↑3 + A*(H↑2) - (E+(A*C))*H - (E*A)
110 D1=H↑3 + (A+D)*(H↑2) + (A*D-E)*H -(E*A)
120 V=((-B)*N)/D1
130 IF V>=0 THEN 170
140 X=P-7
150 IF X>0 THEN 190
160 GO TO 80
170 PRINT V, TAB(30),P
180 GO TO 80
190 PRINT "END OF CALCULATIONS"
200 END
```

```
RUN TITR1

 8K
.19407726                    3.00975762
.739318196                   3.31073333
1.607182                     3.61170914
3.10031864                   3.9126849
5.55210606                   4.21366067
9.10084005                   4.51463643
13.3493431                   4.81561219
17.4066554                   5.11658795
20.5240076                   5.41756372
22.5421029                   5.71853948
23.7075563                   6.01951524
24.336648                    6.320491
24.6638825                   6.62146677
24.830836                    6.92244253
24.9151943                   7.22341829
24.957652                    7.52439405
24.979062                    7.82536981
24.9900347                   8.12634558
24.9960329                   8.42732134
25.0000496                   8.7282971
25.0040919                   9.02927286
25.0101815                   9.33024863
25.0213661                   9.63122439
25.0432503                   9.93220015
25.0868258                   10.2331759
25.1740792                   10.5341516
25.3494378                   10.8351274
25.7038263                   11.1361032
26.4277668                   11.4370789
27.9394798                   11.7380547
31.2461742                   12.0390304
39.2757244                   12.3400062
64.9608534                   12.640982
423.050333                   12.9419577
END OF CALCULATIONS

  200,  NORMAL EXIT FROM PROG.

TIME:     0.318 SEC.
```

statement has been executed, the statement with the next-higher number is then executed. However, you as the programmer may change the sequence of operations by using the GO TO or IF ··· THEN statements:

¶The statement

```
GO TO 80
```

will be followed by execution of the statement numbered 80. Then the program will follow sequentially the statements that follow statement 80.

¶The statement

```
IF X>=0 THEN 190
```

transfers the program to statement 190 *if* the numerical value of the variable X is greater than or equal to zero. Otherwise, the program moves along in order to the statement next in numerical order following the IF ··· THEN statement.

You can add spaces within a statement, almost at your own convenience, in order to make the typewritten statement more readable to you. If there is doubt in your mind about the order in which the computer will perform the indicated arithmetic within a statement, then add some clarifying parentheses; parentheses have the same meaning in BASIC as in arithmetic and algebra. You must always use a closing parenthesis with each opening parenthesis.

Statements 80 – 180 constitute a *computation loop*. This loop is the heart of this particular BASIC program. A large value (larger than will be encountered in the actual titration) for (H^+) is assumed in statement 70. Then this value is reduced to 50% of its previous value in statement 80, the pH value is calculated

for future reference, and then (H^+) is substituted into Equation 16. A value of the titrant volume is calculated, and this value is tested in two IF ··· THEN statements to see if it is negative, or positive or zero; and if it is negative, whether the titration is in the acidic or basic region. Only positive values of volume are acceptable as having any chemical meaning. Negative values are encountered at the beginning of the calculations, and here the computation loop cycles without any output being printed. When (H^+) gets small enough to produce a positive (or zero) value of the titrant volume, the cycle begins to include the PRINT statement, and output gets typed. Finally, when (H^+) becomes smaller than its value in the titrant itself, the calculations pass outside the realm of chemical reality, the volume as calculated becomes negative, and the program is terminated.

It is necessary that each program have a name. It was decided to call this program TITR1, and so the line

```
NAME TITR1
```

was typed prior to the typing of the statements of BASIC Program A. In order to get a listing of the program, one types

```
LIST TITR1
```

To execute the program, one types

```
RUN TITR1
```

The results of executing the program are presented on page 94. The entry 8K is printed automatically, indicating the amount of storage space that the computer has available for running this program. The output is a listing of paired values of V_{NaOH} and pH for evenly-spaced values of (H^+).

After inspecting the typewritten output, you might decide that you want the simulated data to be more closely spaced, and that you have no need for data beyond V_{NaOH} = 23 mℓ. You can get closer spacing by changing the value of the variable I. This is easily accomplished by typing the line

```
60 I=.7
```

The result is that the former statement 60 is replaced by this new statement 60. One way to end the program at 23 mℓ is to add a new statement:

```
125 IF V>=23 THEN 190
```

Typing this statement adds it to the program. To check the program after making the change and the addition, we call for a listing of the program:

```
LIST TITR1

10 A=1.75E-5
20 B=25
30 C=.1
40 D=.1
50 E=1.01E-14
60 I=.7
70 H=1
80 H=H*I
90 P=-(LOG(H))/2.303
100 N=H↑3 + A*(H↑2) - (E+(A*C))*H - (E*A)
110 D1=H↑3 + (A+D)*(H↑2) + (A*D-E)*H -(E*A)
120 V=((-B)*N)/D1
125 IF V>=23 THEN 190
130 IF V>=0 THEN 170
140 X=P-7
150 IF X>0 THEN 190
160 GO TO 80
170 PRINT V, TAB(30),P
180 GO TO 80
190 PRINT "END OF CALCULATIONS"
200 END
```

We can then run the program by typing the instruction

```
RUN TITR1
```

which is the instruction to run the edited program. The output

of the program is as follows:

```
RUN TITR1

OK
9.19849384E-2                2.942607
.33438278                    3.09748105
.616408749                   3.25235511
.909502251                   3.40722916
1.43013252                   3.56210321
2.04068329                   3.71697727
2.84840668                   3.87185132
3.90104676                   4.02672537
5.23776234                   4.18159942
6.87524774                   4.33647348
8.79210319                   4.49134753
10.9136577                   4.64622158
13.1409387                   4.80109564
15.3226125                   4.95596969
17.3365122                   5.11084374
19.0926658                   5.2657178
20.5495796                   5.42059185
21.7990571                   5.5754659
22.6016824                   5.73033995
END OF CALCULATIONS

  200,  NORMAL EXIT FROM PROG.

TIME:     3.274 SEC.
```

When a chemist is involved in a research project for the determination of the numerical value of an equilibrium constant, he or she must be concerned with the precision and the accuracy of that value. How many significant figures can be justified in reporting an equilibrium constant? The answer is not a simple one, but one important piece of information required for the answer is the answer to this second question: what is is smallest change in an assumed value of K_{HA} that causes an experimentally-detectable change in simulated values of V_{NaOH} and pH? We can easily get such information by repeating this simulation with different values of K_{HA}; that is, we can rerun this BASIC program with a slightly-changed value of A, and check the output to see

if there are any significant changes in the predicted volumes for identical values of pH. The value of A is readily changed simply by retyping statement 10, and then the program is run simply by typing the RUN command. The commands and the results for a change of K_{HA} from 1.75×10^{-5} to 1.76×10^{-5} are as follows:

```
10 A=1.76E-5
RUN TITR1

 OK
9.40881534E-2                 2.942607
.337358772                    3.09740175
.620592737                    3.25235511
.975336028                    3.40722916
1.43017729                    3.56210321
2.05161339                    3.71697727
2.86296411                    3.87185132
3.9199317                     4.02672537
5.26144359                    4.18159942
6.90371024                    4.33647348
8.82461747                    4.49134753
10.9537108                    4.64622158
13.1764949                    4.80109564
15.3563779                    4.95596969
17.3667504                    5.11084374
19.118325                     5.2657178
20.5703786                    5.42059186
21.7253007                    5.5754659
22.6140044                    5.73033995
END OF CALCULATIONS

  200,  NORMAL EXIT FROM PROG.

TIME:     0.265 SEC.
```

Comparison of these numbers with the output listed on the previous page reveals that the predicted volumes differ generally only by ±.02 mℓ, an amount comparable to the uncertainty in reading a burette. A closer look shows that the largest differences occur near the macroscopic half-equivalence point, suggesting that such mid-titration data are most useful in evaluating an equilibrium constant.

USE OF A BASIC PROGRAM FROM PERMANENT STORAGE

The easiest way to use a time-sharing terminal is to call a program that someone else has written and placed in permanent storage. You don't need to know anything about programming language, and you don't need to know what the program is doing. Of course, there is the possibility that you therefore won't know what the output means! BASIC Program B is such a program. It performs the same calculations as BASIC Program A. In order to obtain the printout of simulated data, the user types the following two commands:

```
FETCH PROGB
RUN PROGB
```

The results of this series of commands are given on page 102. The FETCH command obtains the program from storage, and places it in the user's active working area, ready for use. (Of course, this procedure only works if BASIC Program B has already been stored in your particular computer system, and if it has been given the name PROGB.) This program is written so that it always has some reasonable numbers supplied for each of the variables and constants. However, if you wish to simulate data for your own special set of conditions, you will want to enter your own numbers. To do this, you merely retype the statements (30, 40, 50, 60, etc.) that are required to define your own experimental conditions. You need a listing of the program in order to identify these statement numbers.

Here you have a program in storage that serves as a starting point for your calculations. It has an output that includes some conventional English-language sentences that describe the set of experimental conditions assumed for the simulation. You can then

B

```
10 PRINT "THIS PROGRAM SIMULATES DATA FROM A ";
20 PRINT "MONOPROTIC ACID TITRATION"
21 PRINT
22 PRINT
30 A=1.75E-5
40 B=25
50 C=.1
60 D=.1
65 E=1.01E-14
70 I=.5
80 H=1.
90 PRINT "A--THE VALUE FOR  (H+)(A-)/(HA)=";A
91 PRINT
100 PRINT "B--THE VOLUME OF THE ORIGINAL COOH SOLUTION=";B
101 PRINT
110 PRINT "C--THE VALUE FOR THE MOLARITY OF THE COOH SOLUTION=";C
111 PRINT
120 PRINT "D- THE VALUE FOR THE MOLARITY OF THE NAOH SOLUTION=";D
121 PRINT
130 PRINT "E--THE VALUE FOR (H+)(OH-)=";E
131 PRINT
140 PRINT "I--THE INCREMENT=";I
141 PRINT
150 PRINT "H--THE VALUE FOR (H+)=";H
151 PRINT
152 PRINT
153 PRINT
160 PRINT "VOLUME OF NAOH",TAB(40),"PH"
161 PRINT
162 PRINT
170 H=H*I
180 P=-(LOG(H))/2.303
190 N=H↑3+A*(H↑2)-(E+(A*C))*H-(E*A)
200 D1=H↑3+(A+D)*(H↑2)+(A*D-E)*H-(E*A)
210 V=((-B)*H)/D1
220 IF V>=0 THEN 260
230 X=P-7
240 IF X>0 THEN 280
250 GO TO 170
260 PRINT V,TAB(40),P
270 GO TO 170
280 PRINT "END OF CALCULATIONS"
290 END
```

THIS PROGRAM SIMULATES DATA FROM A MONOPROTIC ACID TITRATION

A--THE VALUE FOR (H+)(A-)/(HA)= 1.75E-5

B--THE VOLUME OF THE ORIGINAL COOH SOLUTION= 25

C--THE VALUE FOR THE MOLARITY OF THE COOH SOLUTION= .1

D- THE VALUE FOR THE MOLARITY OF THE NAOH SOLUTION= .1

E--THE VALUE FOR (H+)(OH-)= 1.01E-14

I--THE DECREMENT= .5

H--THE VALUE FOR (H+)= 1

VOLUME OF NAOH	PH
.194077263	3.00975762
.739318196	3.31073338
1.607182	3.61170914
3.10031864	3.9126849
5.55210606	4.21366067
9.10084005	4.51463643
13.3493431	4.81561219
17.4066554	5.11658795
20.5240076	5.40756372
22.5421029	5.71853948
23.7075563	6.01951524
24.336648	6.320491
24.6638825	6.62146677
24.830836	6.92244253
24.9151943	7.22341829
24.957652	7.52439405
24.979062	7.82536981
24.9900347	8.12634558
24.9960329	8.42732134
25.0000496	8.7282971
25.0040919	9.02927286
25.0101815	9.33024863
25.0213661	9.63122439
25.0432503	9.93220015
25.0868258	10.2331759
25.1740792	10.5341516
25.3494378	10.8351274
25.7038263	11.1361032
26.4277668	11.4370789
27.9394798	11.7380547
31.2461742	12.0390304
39.2757244	12.3400062
64.9608534	12.640982
423.050333	12.9419577

END OF CALCULATIONS

modify the program to suit your own purposes by adding, changing, or deleting statements. Happily, the original program in storage remains unaffected by anything that you do to its copy.

We have used the PRINT command in several ways. The statement

```
■■■ PRINT "MONOPROTIC ACID"
```

results in the printing of the words MONOPROTIC ACID, followed by advance of the paper to the next line. The statement

```
■■■ PRINT
```

advances the paper one line. The statement

```
■■■ PRINT X
```

results in the printing of the numerical value of the variable X. The number is printed with nine significant figures, except that trailing zeros are not printed. The empty spaces at the extreme right end of the numbers printed on page 102 represent zeros. If a number happened to have only zeros following the decimal point, the decimal point would be omitted, and the number would appear as an integer. The typewriter's tabulation capability can also be used by inserting the command TAB(N) within the PRINT statement; this results in the typewriter "tabbing" across the line. The computer considers the typewriter set with the left-hand margin at column 0. The command TAB(N) causes the next character to be typed in column N. N can be either a number or an arithmetic expression.

PLOTTING WITH AN OUTPUT PRINTER USING BASIC

The listings of numbers that result from BASIC Programs A and B have many more significant figures than are needed for any purpose involving a comparison

with experimental data. Despite this superabundance of digits, however, the lists do not necessarily convey the full significance of the calculations. An overall picture of the calculations is often seen better if the data are graphed. A graphic presentation can be produced by a conventional typewriter or teletype printer. Such a graph is rather crude, since the coordinates of each point must of necessity be positions on the paper where a character can be typed. Notwithstanding this limitation, such plots can be informative, and we shall present two programs that produce graphical output of a titration simulation.

BASIC Program C illustrates a simple plotting program. Very similar to BASIC Program A, this program gives output via the statement

```
170 PLOT 10+V="*", 10="+"
```

The PLOT statement is executed from right to left, so that the first command is to plot 10="+". This means that the typewriter is to type a + sign in column 10. And then, without advancing the paper, the command to plot 10+V="*" is executed. This means that the typewriter is to plot the symbol * in column 10+V. Finally, when all the characters have been typed, the paper is advanced to the next line. In order to have pH plotted along the vertical axis, the calculation loop has been instructed to change pH by increments of 0.5 pH units, thus making each print line on the graph correspond to 0.5 pH units. The horizontal axis is the V_{NaOH} axis. We used 50 spaces (50 character columns) for this graph, and the volume range was from 0 to about 50 mℓ, so we were able to let each space equal one volume unit. Otherwise, we

C

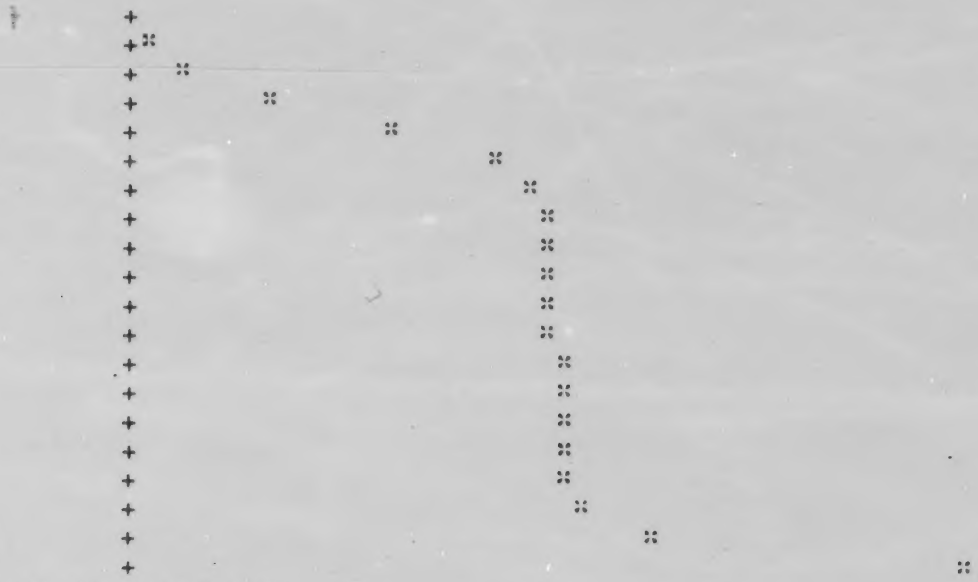
```
LIST PROGC

10 A=1.75E-5
20 B=25
30 C=.1
40 D=.1
50 E=1.01E-14
60 I=.5
70 P=1
80 P = P+I
90 H=10↑(-P)
100 N=H↑3 + A*(H↑2) - (E+(A*C))*H - (E*A)
110 D1=H↑3 + (A+D)*(H↑2) + (A*D-E)*H - (E*A)
120 V=((-B)*N)/D1
130 IF V>=0 THEN 170
140 X = P-7
150 IF X>0 THEN 190
160 GO TO 80

170 PLOT 10+V="*", 10="+"
180 GO TO 80
190 PRINT "END OF CALCULATIONS"
200 END

RUN PROGC

 8K
```



```
END OF CALCULATIONS

  200,  NORMAL EXIT FROM PROG.

TIME:     0.218 SEC.
```

would have been required to multiply the variable by an appropriate scaling factor so that the graph would fit into the allotted space on the paper.

BASIC Program D is written for permanent storage, and has several useful features. The output begins with a title, and a listing of the numerical values of the various constants that characterize the particular acid being titrated and the experimental conditions of the titration being simulated. The actual plot has labelled axes, and an indication (with the printing of the symbol X) of the half-equivalence point. This program can be called from storage and used without understanding the various plotting statements, modifying computation statements as desired in the same manner as described on the previous pages. However, there are some additional programming features which may be of interest.

Use of a *subroutine* is illustrated in statements 424 to 430. These statements are a miniprogram to plot an X at the half-equivalence point. The final statement is RETURN. Execution gets transfered to the subroutine by the command

```
GOSUB 424
```

After completion of the calculations or instructions of the subroutine, the execution returns to the statement immediately following the GOSUB statement.

For this graph, it was decided to use a scaling factor to expand the horizontal axis. Can you find where the scaling factor is inserted?

In order to get the vertical axis labelled with pH values,

D

```
10 A=1.75E-5
20 B=25
30 C=.1
40 D=.1
50 E=1.008E-14
60 I=.5
65 H=1
70 PRINT "PLOT OF A SIMULATED MONOPROTIC ACID TITRATION CURVE ";
71 PRINT "WITH  (H+)(A-)/(HA)=";A
72 PRINT
73 PRINT
80 PRINT "A--THE VALUE FOR  (H+)(A-)/(HA)=";A
81 PRINT
90 PRINT "B--THE VOLUME OF THE ORIGINAL COOH SOLUTION=";B
91 PRINT
100 PRINT "C--THE VALUE FOR THE MOLARITY OF THE COOH SOLUTION=";C
101 PRINT
110 PRINT "D--THE VALUE FOR THE MOLARITY OF THE NAOH SOLUTION=";D
111 PRINT
120 PRINT "E--THE VALUE FOR (H+)(OH-)=";E
121 PRINT
130 PRINT "I--THE DECREMENT=";I
131 PRINT
140 PRINT "H--THE VALUE FOR (H+)=";H
141 PRINT
150 PRINT
160 PRINT
170 PRINT TAB (15),"MILLILITERS OF SODIUM HYDROXIDE"
180 PRINT "PH"
190 PRINT TAB (10),"0          5         10         15         20         25"
200 PRINT TAB (10),"+----+----+----+----+----+----+----+----+----+----+"
210 FOR W= 1 TO 10
220 PRINT TAB(10),"+"
230 NEXT W
235 X=0
240 H=H*I
245 IF H>A THEN 250
246 GOSUB 424
250 P=-(LOG(H))/2.303
260 P1=INT(10*P)/10
270 P2=INT(P)
280P=P/2
290 N=H↑3+A*(H↑2)-(E+(A*C))*H-(E*A)
300 D1=H↑3+(A+D)*(H↑2)+(A*D-E)*H-(E*A)
310 V=((-B)*N)/D1
320IF V>=0 THEN.360
330 X=P-7
340 IF X>0 THEN 420
350 GO TO 240
360 IF P1<>P2 THEN 400
361 IF P1 <=9 THEN370
362 PRINT P1;
```

```
363 PLOT 6+(2*V)+.5="*",5="+"
364 GO TO 240
370 PRINT P1;
380 PLOT 7+(2*V)+.5="*",6="+"
390 GO TO 240
400 PLOT 10 +(2*V)+.5="*",9="+"
410 GO TO 240
420 PRINT "END OF CALCULATIONS"
421 GO TO 431
424 IF X=1 THEN 430
425 X=1
426 P=-(LOG(A))/2.303
427 V1=.5*B*C/D
428 PLOT 9+(2*V1)="X",9="+"
430 RETURN
431 END
```

OUTPUT

```
PLOT OF A SIMULATED MONOPROTIC ACID TITRATION CURVE
WITH  (H+)(A-)/(HA)= 1.75E-5

A--THE VALUE FOR  (H+)(A-)/(HA)= 1.75E-5

B--THE VOLUME OF THE ORIGINAL COOH SOLUTION= 25

C--THE VALUE FOR THE MOLARITY OF THE COOH SOLUTION= .1

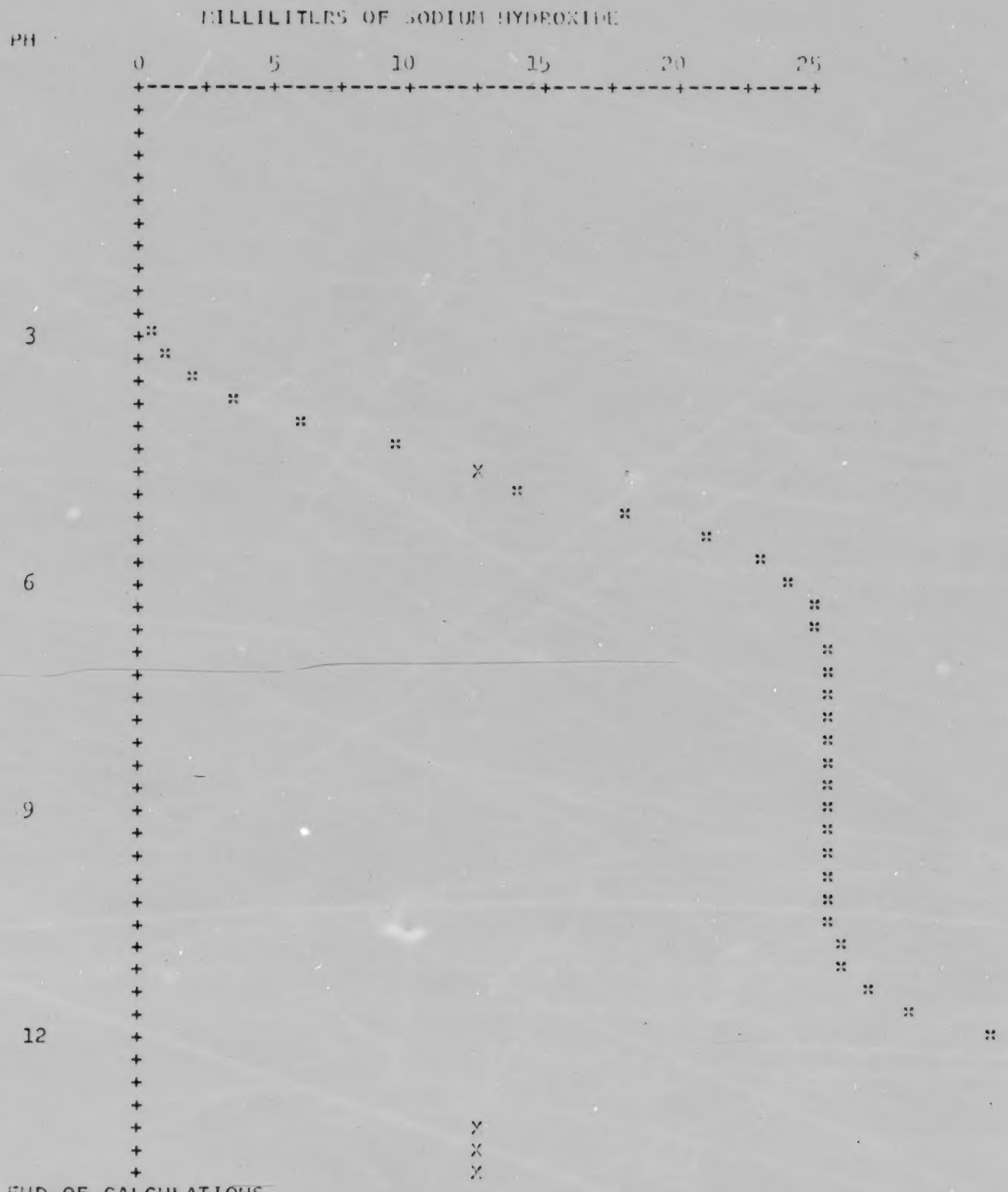
D--THE VALUE FOR THE MOLARITY OF THE NAOH SOLUTION= .1

E--THE VALUE FOR (H+)(OH-)= 1.008E-14

I--THE DECREMENT= .5

H--THE VALUE FOR (H+)= 1
```

OUTPUT CONTINUED ON NEXT PAGE



END OF CALCULATIONS

431, NORMAL EXIT FROM PROG.

TIME: 0.598 SEC.

it was necessary to have integral values of pH available. To do this, use was made of the INT(X) command to convert a variable into its next-lowest integer (the number rounded off to an integer by simply discarding all digits following the decimal point). This program is presented to illustrate the sorts of programming niceties that can be used to dress up the output of a printer-generated graph. You may have other ideas.

CONFRONTATION OF SIMULATED DATA AND EXPERIMENTAL DATA FOR A TITRATION

BASIC Program E provides a point-by-point comparison of experimental data from a titration experiment with the predictions of a mathematical model for that experiment. The program is written for permanent storage. When run, the program provides for a dialogue between computer and user, with instructions coming from the computer in the form of English-language questions and statements. In the interest of simplicity, and in the interest of getting the user involved in the actual program, this interactive dialogue has been kept to a rather minimal level, but you may wish to write a more extensive program with more conversational interaction.

The program begins with a dimension statement

```
10 DIM A(50),B(50)
```

that reserves storage space for 50 paired numbers A_i,B_i; that is, for 50 subscripted variables that will be identified with the experimental values of pH and V_{NaOH}. Within the program, the subscripted variables are written as A(X) and B(X), where identical values of X means that the two variables are paired. Statement 60 prints a question that asks the user to type a number that

tells the computer how many sets of pairs $\{pH, V_{NaOH}\}$ are to be entered. The following statement

```
70 INPUT N
```

orders a pause in the execution of the program until a number has been entered by the user at the terminal. That number becomes the value of the variable N, and the statements numbered 90 through 140 then ask for values of pH and V_{NaOH} a total of N times, storing the entered numbers as an array of the form

A(1), B(1)

A(2), B(2)

A(3), B(3)

A(4), B(4)

. . .

A(N), B(N)

The program now proceeds to take each of these pairs in turn, calculating a predicted value of the volume that corresponds to the experimental pH value, and then printing the predicted and experimental values of the titrant volume for comparison.

In order to perform the calculations, it is necessary to have values for the two equilibrium constants, the two molarities, and the initial volume of acid. *These numbers have already been entered by statement 160.* You might wish to alter the program by deleting statement 160 from the program, allowing yourself the option of entering these numbers during the execution of the program. You would need a statement prior to statement 150 that printed out an appropriate question to indicate the form in which these constants are to be entered from the keyboard.

E

```
10 DIM A(50),B(50)
20 PRINT "THIS PROGRAM CONFRONTS EXPERIMENTAL DATA"
30 PRINT "WITH THE PREDICTIONS OF A MATHEMATICAL MODEL"
35 PRINT "FOR THE TITRATION OF A MONOPROTIC ACID"
40 PRINT
50 PRINT
60 PRINT "HOW MANY SETS OF EXPERIMENTAL DATA WILL YOU BE USING";
70 INPUT N
80 PRINT
90 FOR X=1 TO N
100 PRINT "PH=";
110 INPUT A(X)
120 PRINT "VOLUME OF NAOH=";
130 INPUT B(X)
140 NEXT X
150 READ A,B,C,D,E
160 DATA 1.75,25,0.1,0.1,1.008
170 A=A*10↑(-5)
180 E=E*10↑(-14)
190 PRINT "THE VALUE FOR (H+)(A-)/(HA)=";A
200 PRINT
210 PRINT "THE VOLUME OF THE ORIGINAL HA SOLUTION=";B
220 PRINT
230 PRINT "THE VALUE FOR THE MOLARITY OF THE HA SOLUTION=";C
240 PRINT
250 PRINT "THE VALUE FOR THE MOLARITY OF THE NAOH SOLUTION=";D
260 PRINT
270 PRINT "THE VALUE FOR (H+)(OH-)=";E
280 PRINT
290 PRINT
300 PRINT TAB(20),"CALCULATED",TAB(40),"EXPERIMENTAL"
310 PRINT "PH",TAB(20),"VOLUME OF NAOH",TAB(40),"VOLUME OF NAOH"
320 PRINT
330 PRINT
340 PRINT
350 FOR X= 1 TO N
360 T=A(X)
370 H=10↑(-T)
380 P=-(LOG(H))/2.303
390 N=H↑3+A*(H↑2)-(E+(A*C))*H-(E*A)
400 D1=H↑3+(A+D)*(H↑2)+(A*D-E)*H-(E*A)
410 V=((-B)*N)/D1
420 IF V>=0 THEN 460
430 X=P-7
440 IF X>0 THEN 480
450 GO TO 470
460 PRINT A(X),TAB(20),V,TAB(40),B(X)
470 NEXT X
480 PRINT "END OF CALCULATIONS"
490 END
```

```
THIS PROGRAM CONFRONTS EXPERIMENTAL DATA
WITH THE PREDICTIONS OF A MATHEMATICAL MODEL
FOR THE TITRATION OF A MONOPROTIC ACID


HOW MANY SETS OF EXPERIMENTAL DATA WILL YOU BE USING?
5


PH=?
3.04

VOLUME OF NAOH=?
.19

PH=?
3.31

VOLUME OF NAOH=?
.74

PH=?
3.62

VOLUME OF NAOH=?
1.73

PH=?
3.89

VOLUME OF NAOH=?
3.12

PH=?
4.34

VOLUME OF NAOH=?
5.55

THE VALUE FOR (H+)(A-)/(HA)= 1.75E-5

THE VOLUME OF THE ORIGINAL HA SOLUTION= 25

THE VALUE FOR THE MOLARITY OF THE HA SOLUTION= .1

THE VALUE FOR THE MOLARITY OF THE NAOH SOLUTION= .1

THE VALUE FOR (H+)(OH-)= 1.008E-14


PH              CALCULATED              EXPERIMENTAL
                VOLUME OF NAOH          VOLUME OF NAOH


 3.04            .240481747              .19
 3.31            .736393441              .74
 3.62            1.63590446              1.73
 3.89            2.95390902              3.12
 4.34            6.90691832              5.55
END OF CALCULATIONS
```

113
109 d

You can change just the value of A (that is, just the value of K_{HA}) by adding a statement of the form

```
161 A=1.76
```

Note that the exponent portion of each equilibrium constant is added later, in statements 170 and 180. This procedure for entering the constants is just one of many possibilities, and you should write the program in the way that is most convenient for you.

A sample of the user—computer dialogue, as well as the calculated comparison of model and data, is presented on page 113.

Certain data points, taken from the region of the titration curve in the vicinity of the half-equivalence point, are most sensitive to variations in the value of K_{HA}, and these are the only points that need to be considered when searching for a value of that equilibrium constant. A final comparison should include data from throughout the whole titration curve.

You may wish to write a program that allows you to try a whole series of different values of K_{HA}, while keeping the experimental data stored for repeated comparisons. Another worthwhile refinement would be to have the program find the difference between calculated and experimental titrant volumes, printing out that difference as a part of the output.

USE OF A WANG 700 PROGRAMMABLE CALCULATOR IN EVALUATING AN EQUILIBRIUM CONSTANT

The Wang 700 calculator is a miniature computer with a limited memory (a limitation) and with extremely simple input-output capability (an advantage). Such a calculator can be of great use to the chemist who is trying to find the numerical value of an equilibrium constant that brings the predictions of a mathematical model into agreement with a few experimental data points clustered about the half-equivalence point of a titration. Wang Program **a** performs such calculations. The user is closely involved with the actual calculations, having close control over the numbers being used in the calculations. The user *interacts* with the calculator and with the calculations in a meaningful and effective manner.

The Wang 700 calculator permits the user to perform arithmetic in the same manner as with any electronic calculator, by entering numbers and depressing keys labelled +, -, ×, ÷, and so forth. Numbers at any stage of the calculations can be stored in one of 122 data registers of the calculator's core memory. The whole sequence of operations that constitutes a program can be stored in memory so that the calculator can then execute the steps automatically. Finally, this program can be stored for future use on a magnetic-tape cassette.

This program is based on Equation 16. The strategy is quite simple: we shall store (in registers 00 to 08) the various terms that need to be added together to give *numerator* and *denominator*, then perform a division at the very end. Since the

a

STEP	KEY	CODE
00	MARK	0408
01	1	0701
02	CLEAR x	0715
03	STOP	0515
04	CHANGE SIGN	0711
05	10^x	0613
06	STORE DIRECT	0404
07	REGISTER 00	0000
08	STORE DIRECT	0404
09	REGISTER 02	0002
10	x^2	0713
11	STORE DIRECT	0404
12	REGISTER 01	0001
13	STORE DIRECT	0404
14	REGISTER 08	0008
15	× DIRECT	0402
16	REGISTER 02	0002
17	CLEAR x	0715
18	STOP	0515
19	× DIRECT	0402
20	REGISTER 08	0008
21	STORE DIRECT	0404
22	REGISTER 03	0003
23	↑	0604
24	RECALL DIRECT	0405
25	REGISTER 00	0000
26	× DIRECT	0402
27	REGISTER 03	0003
28	+	0600
29	1	0701
30	4	0704
31	CHANGE SIGN	0711
32	10^x	0613

STEP	KEY	CODE
33	×	0602
34	↓	0605
35	STORE DIRECT	0404
36	REGISTER 04	0004
37	RECALL DIRECT	0405
38	REGISTER 03	0003
39	STORE DIRECT	0404
40	REGISTER 05	0005
41	CLEAR x	0715
42	STOP	0515
43	× DIRECT	0402
44	REGISTER 05	0005
45	CLEAR x	0715
46	STOP	0515
47	× DIRECT	0402
48	REGISTER 01	0001
49	× DIRECT	0402
50	REGISTER 03	0003
51	CLEAR x	0715
52	STOP	0515
53	STORE DIRECT	0404
54	REGISTER 07	0007
55	RECALL DIRECT	0405
56	REGISTER 02	0002
57	↑	0604
58	RECALL DIRECT	0405
59	REGISTER 08	0008
60	+	0600
61	RECALL DIRECT	0405
62	REGISTER 04	0004
63	-	0601
64	↓	0605
65	STORE DIRECT	0404

STEP	KEY	CODE
66	REGISTER 06	0006
67	↑	0604
68	RECALL DIRECT	0405
69	REGISTER 01	0001
70	+	0600
71	RECALL DIRECT	0405
72	REGISTER 03	0003
73	+	0600
74	↓	0605
75	STORE DIRECT	0404
76	REGISTER 09	0009
77	RECALL DIRECT	0405
78	REGISTER 06	0006
79	↑	0604
80	RECALL DIRECT	0405
81	REGISTER 05	0005
82	-	0601
83	RECALL DIRECT	0405
84	REGISTER 09	0009
85	÷	0603
86	RECALL DIRECT	0405
87	REGISTER 07	0007
88	CHANGE SIGN	0711
89	×	0602
90	STOP	0515
91	END PROGRAM	0512

SAMPLE OUTPUT OF THE PROGRAM

$K_{HA} = 1.75 \times 10^{-5}$, $M_{NaOH} = 0.1000$, $M_{HA} = 0.1000$, $V_{HA} = 25.00$

pH =	V_{NaOH} =
3.009	0.192···
3.310	0.736
3.611	1.602
3.912	3.091
4.213	5.538
4.514	9.081

USER'S OPERATING INSTRUCTIONS	PROGRAM STEP INVOLVED
depress SEARCH, then 0	00
depress GO	goes to 03 and stops
enter value of pH, then GO	goes to 18 and stops
enter value of K_{HA}, then GO	goes to 42 and stops
enter value of M_{HA}, then GO	goes to 46 and stops
enter value of M_{NaOH}, then GO	goes to 52 and stops
enter value of V_{HA}, then GO	goes to 89, stops, with displayed value of V_{NaOH}.

STORAGE LOCATIONS AT TIME OF FINAL CALCULATIONS	
Register 00	(H^+)
Register 01	$M_{NaOH}(H^+)^2$
Register 02	$(H^+)^3$
Register 03	$M_{NaOH}K_{HA}(H^+)$
Register 04	$K_w\{K_{HA} + (H^+)\}$
Register 05	$M_{HA}K_{HA}(H^+)$
Register 06	*numerator*
Register 07	V_{HA}
Register 08	$K_{HA}(H^+)^2$

calculations are designed for data in the region of the half-equivalence point where predicted values of V_{NaOH} are insensitive to the assumed value of K_w, we shall always use the value

$$K_w = 1.00 \times 10^{-14}$$

Certain keys on the Wang keyboard need an explanation, for they are used to move numbers in and out of the storage registers.

STORE DIRECT. This key is followed by a register key, and the result is that the number that is displayed in the x-register on the calculator (displayed in nixie lights) is stored in the indicated register. The number also remains in the x-register, available for further computation.

RECALL DIRECT. When this key is followed by a register key, the contents of that register become displayed in the x-register, ready for further computation. The number remains stored, and can be recalled as many times as desired.

× DIRECT. When followed by a register key, this command multiples the contents of that indicated register by the contents of the displayed x-register, and stores the product in the indicated register. There is now a new number in the storage register, the result of the multiplication. The displayed number in the x-register remains unchanged.

+, -, ×, ÷. Adds, subtracts, multiplies, or divides the numbers displayed in the x- and y-registers, and places the result in the y-register. In subtraction, the order is y-x; in division the operation is y/x.

↑. Places the contents of the x-register into the y-register, leaving the x-register unchanged.

↓. Places the contents of the y-register into the x-register, leaving the y-register unchanged.

↑↓. Interchanges the contents of the x- and y-registers.

If you want to become more familiar with programming and using the Wang calculator, try to modify Wang Program a to get some of the following features:

• *Write a program that permits entry of assumed values of the equilibrium constant* K_w.

• *Write a program that retains the values of* M_{NaOH}, M_{HA}, *and* V_{NaOH}, *so that these values do not have to be entered each time a new value of* pH *or* K_{HA} *is chosen.*

• *Write a program that allows the entry of repeated values of* pH *with the same values of all the constants, so that several pieces of experimental data can be compared with the predictions of the model without re-entry of constants.*

Output from the Wang is in the form of a display of nixie lights, so the user must write down these numbers before proceeding to the next calculation. While this may appear to be more demanding than simply watching a high-speed printer or a Selectric typewriter produce numerical output, it does have an advantage: the user becomes more involved with the calculations, and has time to think about the meaning of the numbers. This can often be a blessing; mistakes can be caught earlier, and misconcenptions can be corrected earlier.

Chapter 2

Titration of a Diprotic Acid

The chemical model for the titration of a diprotic carboxylic acid involves an additional chemical equilibrium. An additional chemical equation appears in the chemical model which in turn introduces an additional algebraic equation into the mathematical model. The equation for the titration curve thus becomes more complicated. Once we have derived the equation for the titration curve, however, this complication need cause no problems or inconveniences in making computer calculations. Indeed, instead of complications, titration of a diprotic acid provides additional insights into the chemistry of coupled reactions and competitive equilibria.

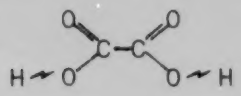
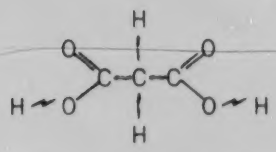
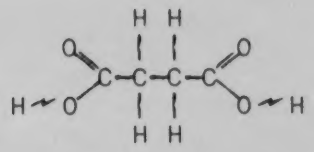
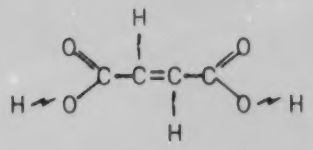
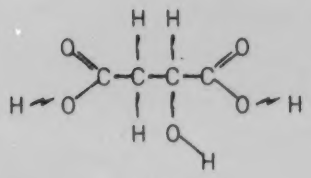
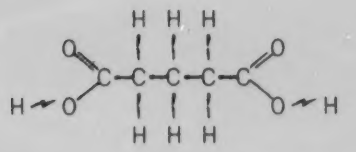
We shall investigate the analysis of experimental titration data for diprotic carboxylic acids by again confronting laboratory titration data with the predictions of our model. We shall also investigate several aspects of the model by performing computer simulations of the model for a variety of different situations.

There are many common diprotic carboxylic acids, a few of which are presented in Table 3. Many are major constituents of certain plants or food products, or of significant biochemical importance. Most of the low-molecular-weight dicarboxylic acids are sufficiently soluble in water so that a titration curve can be obtained without difficulty. Some of these acids have been studied in great detail, but the equilibria for others have been investigated only in passing, and some research topics of interest can be found within this class of rather simple compounds.

We shall begin this chapter with a statement of the chemical

Table 3

STRUCTURES OF SOME DIPROTIC CARBOXYLIC ACIDS

	oxalic acid
	malonic acid
	succinic acid
	*trans* isomer: fumaric acid *cis* isomer: maleic acid
	malic acid
	glutaric acid

and mathematical models that we shall use for simulating diprotic acid equilibria in solution.

THE CHEMICAL MODEL FOR OUR SIMULATION OF THE TITRATION OF A DIPROTIC ACID

Any one of the representative diprotic carboxylic acids represented by structural formulas in Table 3 can be represented as an associated acid H_2A which can lose one or two protons in solution to become anions HA^- or $A^=$. In a solution prepared by mixing quantities of the acid, the salts NaHA and Na_2A, sodium hydroxide, and water, the species present (we shall assume) are

$$H_2O,\ H_2A,\ HA^-,\ A^=,\ Na^+,\ H^+,\ OH^-$$

We require a sufficient number of chemical equilibria in our model to permit the interconversion of all A-containing species, as well as the dissociation of the solvent water. We shall assume the following three chemical equilibria:

$$H_2O \rightleftarrows H^+ + OH^- \tag{44}$$

$$H_2A \rightleftarrows HA^- + H^+ \tag{45}$$

$$HA \rightleftarrows A^= + H^+ \tag{46}$$

This listing of the chemical species assumed, together with this listing of the chemical equilibria assumed, constitutes the *chemical model for the system.*

THE MATHEMATICAL MODEL FOR OUR SIMULATION OF A DIPROTIC ACID TITRATION

Associated with each of the chemical reactions of the chemical model is an equilibrium-constant equation. Thus we write the algebraic equations

$$K_w = (H^+)(OH^-) \tag{47}$$

$$K_{H_2A} = \frac{(H^+)(HA^-)}{(H_2A)} \tag{48}$$

$$K_{HA^-} = \frac{(H^+)(A^=)}{(HA^-)} \qquad (49)$$

The requirement of electrical neutrality of the solution gives us the equation

$$2(A^=) + (HA^-) + (OH^-) = (H^+) + (Na^+) \qquad (50)$$

Notice the coefficient "2" that appears so that two negative charges will be counted for each $A^=$ anion in solution. Finally, we include two conservation equations in our mathematical model:

$$[A] = (H_2A) + (HA^-) + (A^=) \qquad (51)$$

$$[Na] = (Na^+) \qquad (52)$$

Equations 47 — 52 suffice to permit elimination of all microscopic species concentrations except for (H^+), giving us an algebraic equation relating [A] and [Na] to (H^+). For the particular experimental situation of the titration of the acid H_2A with the base NaOH, it is convenient to change variables by introducing the two equations

$$[A] = \frac{V_{H_2A} M_{H_2A}}{V_{H_2A} + V_{NaOH}} \qquad (53)$$

$$[Na] = \frac{V_{NaOH} M_{NaOH}}{V_{H_2A} + V_{NaOH}} \qquad (54)$$

Equations 47 — 54 constitute a set of simultaneous algebraic equations that can be combined to give an equation that relates the two experimental variables (H^+) and V_{NaOH}. The equation is

$$V_{NaOH} = -V_{HA}\left(\frac{numerator}{denominator}\right) \qquad (55)$$

where the quantities *numerator* and *denominator* are given by the relations

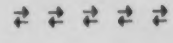
$$\text{numerator} = (H^+)^4 + K_{H_2A}(H^+)^3 + \{K_{H_2A}K_{HA^-} - K_{H_2A}M_{H_2A} - K_w\}(H^+)^2 + \{-2K_{H_2A}K_{HA^-}M_{H_2A} - K_wK_{H_2A}\}(H^+) - K_wK_{HA^-}K_{H_2A}$$

$$\text{denominator} = (H^+)^4 + \{K_{H_2A} + M_{NaOH}\}(H^+)^3 + \{K_{H_2A}K_{HA^-} + K_{H_2A}M_{NaOH} - K_w\}(H^+)^2 + \{K_{H_2A}K_{HA^-}M_{NaOH} - K_wK_{H_2A}\}(H^+) - K_wK_{H_2A}K_{HA^-}$$

Equation 55 is the heart of all the computer calculations in this chapter.

• *Perform the algebra that consolidates the information of Equations 47 — 54 into Equation 55.*

• *Compare Equations 16 and 55. On the basis of this comparison, predict the form (and some or all of the details) of the corresponding equation for a triprotic acid. How would you verify your prediction?*



PREDICTIONS OF THE MODEL FOR THE TITRATION OF A DIPROTIC ACID

Again we shall present two different methods of using an IBM 1130 computer to simulate the titration of an acid with a base in aqueous solution. Computer programs will be presented with output both as a tabulation of numbers and as a graph of titrant volume versus pH. We shall assume, for purposes of discussing these programs, that values of the various equilibrium constants have been obtained in some way. In the next section, we shall show that *the partial-equivalence point method*, an extension of the half-equivalence point method, is an adequate method for estimating a trial value of dissociation constants for diprotic acids in most cases, and an excellent method in some cases.

PREDICTIONS OF THE MODEL PRESENTED AS A TABLE OF pH AND VOLUME VALUES

FORTRAN Program 9 utilizes Equation 55 for its calculation of the titrant volume that corresponds to various values of (H^+). The program begins with $(H^+) = 1.00$, and then systematically reduces the value of (H^+) with the statement

```
H = .8*H
```

a statement that replaces the value of the variable H by 80% of its value. When the assumed value of (H^+) is larger than possible in the titration, Equation 55 yields a negative value of the titrant volume. Such a situation is chemically impossible, and we reject all such pairs of (H^+),V_{NaOH} values with the statement

```
IF (VMOH) 2, 20, 20
```

9

```
// JOB                  S71007,S51


// FOR
* LIST SOURCE PROGRAM
*IOCS(CARD, 1132 PRINTER)

C      TITRATION CURVE
C      PREDICTIONS OF THE CHEMICAL MODEL
C      DIPROTIC ACID

       REAL KHA, KHHA, KW, NUM, MHA, MMOH
       VHA = 25.00
       MHA = 0.0500
       MMOH = 0.1000
       KHHA = 1.E-6
       KHA = 1.E-7
       KW = 1.008E-14

       H = 1.
     1 H = .8*H
       PH = -(ALOG(H))/2.303
       NUM = H**4 + KHHA*(H**3) + (KHHA*KHA - KHHA*MHA - KW)*(H**2)
      *-(2*KHHA*KHA*MHA + KW*KHHA)*H - KW*KHA*KHHA
       DEN = H**4 + (KHHA + MMOH)*(H**3) + (KHHA*KHA + KHHA*MMOH - KW)
      **(H**2) + (KHHA*KHA*MMOH - KW*KHHA)*H - KW*KHA*KHHA
       VMOH = -VHA*NUM/DEN
       IF (VMOH) 2, 20, 20
     2 IF (PH - 7.00) 1, 1, 30
    20 WRITE (3,10) VMOH, PH
    10 FORMAT (F10.3, F10.3)
       GO TO 1
    30 CALL EXIT
       END

// XEQ
```


147

0.008	3.681
0.033	3.778
0.060	3.875
0.089	3.972
0.124	4.069
0.164	4.166
0.212	4.263
0.270	4.360
0.341	4.457
0.428	4.553
0.535	4.650
0.666	4.747
0.825	4.844
1.020	4.941
1.256	5.038
1.541	5.135
1.882	5.232
2.286	5.329
2.760	5.425
3.310	5.522
3.940	5.619
4.651	5.716
5.439	5.813
6.300	5.910
7.225	6.007
8.203	6.104
9.223	6.201
10.273	6.298
11.342	6.394
12.421	6.491
13.501	6.588
14.572	6.685
15.625	6.782
16.650	6.879
17.635	6.976
18.568	7.073
19.439	7.170
20.238	7.266
20.960	7.363
21.601	7.460
22.163	7.557
22.648	7.654
23.062	7.751
23.411	7.848
23.703	7.945
23.945	8.042
24.145	8.138
24.309	8.235
24.442	8.332
24.551	8.429
24.639	8.526
24.711	8.623
24.769	8.720
24.815	8.817
24.853	8.914
24.884	9.011
24.909	9.107
24.930	9.204
24.948	9.301
24.963	9.398
24.976	9.495
24.988	9.592
24.999	9.689
25.010	9.786
25.022	9.883
25.035	9.979
25.050	10.076
25.067	10.173
25.087	10.270
25.112	10.367
25.143	10.464
25.181	10.561
25.228	10.658
25.287	10.755
25.360	10.851
25.452	10.948
25.567	11.045
25.712	11.142
25.894	11.239
26.122	11.336
26.411	11.433
26.777	11.530
27.241	11.627
27.834	11.724
28.594	11.820
29.574	11.917
30.852	12.014
32.536	12.111
34.789	12.208
37.866	12.305
42.188	12.402
48.506	12.499
58.296	12.596
74.933	12.692
108.185	12.789
203.028	12.886
2050.708	12.983

which transfers the program back to statement 1 (by way of statement 2) if the volume is negative, and allows output of the calculated value of titrant volume only if that volume is zero or positive. Statement 2 checks to be sure that the negative volume has been encountered early in the titration; if the pH value has passed 7 and the titration has been proceeding, a negative volume signals that we have assumed a value of (H^+) that is less than chemically possible, that we have assumed a value of (H^+) lower than the value in pure titrant. Such an event is the sign that all meaningful calculation has been completed, and that it is time to stop. Transfer of the program to statement 30 calls exit and end of the program. Output of the program, with the particular set of equilibrium constants and initial concentrations and volume give in the program listing, is presented on page 124.

• *Write a computer program that presents output as evenly-spaced* pH *values.*

• *Here's a challenge! Write a computer program that gives output as evenly-spaced* V_{NaOH} *values.*

Note that the algebraic expression for NUM is too long to fit on a single punch card, and so it was continued to a second card. A character punched in column 6 indicates that such a card contains a continuation of the previous card. The statement gets typed on the program listing as a two-line statement, but gets executed as if it were all printed on a single (extra-long) line.

As expected, the equivalence point occurs at 25.00 mℓ when

25.00 mℓ of a diprotic acid of molarity 0.0500 moles/liter is titrated with a sodium hydroxide solution of twice that molarity. The criterion for equivalence is that *twice as many moles of base must be added to a given number of moles of acid.* Why "twice"?

ON SEEING TWO ENDPOINTS IN THE TITRATION OF A DIPROTIC ACID

The number of endpoints that can be observed during the titration of a diprotic acid with a solution of sodium hydroxide depends on the numerical values of the two dissociation constants of the acid, as well as on the values of the molarities of the acid and titrant solutions. On the following pages, we shall examine the results of some numerical calculations simulating the titration of several hypothetical acids in order to gain insight into the effect of the values of K_{H_2A} and K_{HA^-} on the shape of the titration curve. We shall focus our attention on the question: *"How many endpoints can be recognized during the titration?"* These calculations are based on Equation 55, and are performed using FORTRAN Program 10. Output for various values of the two equilibrium constants is presented on pages 128 — 133.

Inspection of the simulated titration curves leads one to propose some generalizations of the following sort:

¶In order to get a sharp first endpoint, there must be a large separation of the numerical values of the K's, probably of the order of at least a factor of 10^4.

¶To achieve a sharp second endpoint, it is necessary to reduce the value of (H^+) to a value much less than the numerical value of K_{HA^-}.

10

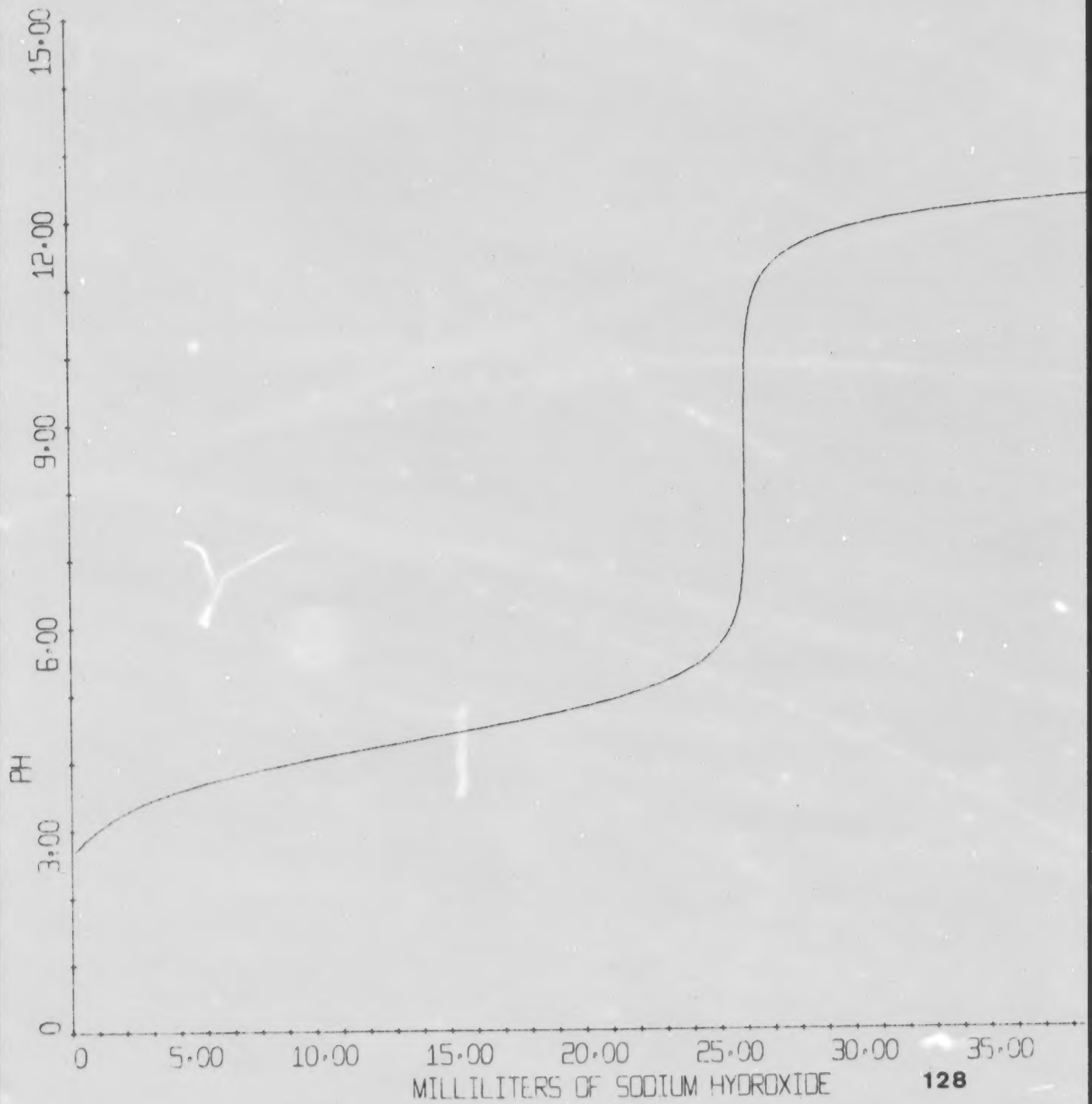
```
// JOB                    S71007,S51


// FOR
* LIST SOURCE PROGRAM
*IOCS(CARD, 1132 PRINTER, TYPEWRITER, PLOTTER)
*ONE WORD INTEGERS
C       ON SEEING TWO ENDPOINTS IN THE TITRATION OF A DIPROTIC ACID
        REAL KHA, KHHA, KW, NUM, MHA, MMOH
        VHA = 25.00
        MHA = 0.0500
        MMOH =  0.1000
        KHHA = 1.E-4
        KHA = 1.E-13
        KW = 1.008E-14
        CALL PREP (.2, .5, 1., 1.)
        WRITE (7,15)
   15 FORMAT ('NUMBER OF ENDPOINTS IN THE TITRATION OF A DIPROTIC ACID')
        H = 1.
    1 H = .5*H
        PH = -(ALOG(H))/2.303
        NUM = H**4 + KHHA*(H**3) + (KHHA*KHA - KHHA*MHA - KW)*(H**2)
       *-(2*KHHA*KHA*MHA + KW*KHHA)*H - KW*KHA*KHHA
        DEN = H**4 + (KHHA+MMOH)*(H**3) + (KHHA*KHA + KHHA*MMOH - KW)
       **(H**2) + (KHHA*KHA*MMOH - KW*KHHA)*H - KW*KHHA*KHA
        VMOH = -VHA*NUM/DEN
        IF (VMOH) 1,2,2
    2 CALL FPLOT (-2,VMOH,PH)
    5 H = H - .1*H
        PH = -(ALOG(H))/2.303
        NUM = H**4 + KHHA*(H**3) + (KHHA*KHA - KHHA*MHA - KW)*(H**2)
       *-(2*KHHA*KHA*MHA + KW*KHHA)*H - KW*KHA*KHHA
        DEN = H**4 + (KHHA+MMOH)*(H**3) + (KHHA*KHA + KHHA*MMOH - KW)
       **(H**2) + (KHHA*KHA*MMOH - KW*KHHA)*H - KW*KHHA*KHA
        VMOH = -VHA*NUM/DEN
        IF (50.-VMOH) 10,3,3
    3 CALL FPLOT (0,VMOH,PH)
        GO TO 5
   10 CALL YAXIS (0., 0., 1., 15, 5)
        WRITE (7,17)
   17 FORMAT ('PH')
        CALL XAXIS (0., 0., 1., 50, 10)
        WRITE (7,16)
   16 FORMAT ('MILLILITERS OF SODIUM HYDROXIDE')
        CALL FINPL
        CALL EXIT
        END

// XEQ
```

NUMERICAL EXPERIMENT IN THE TITRATION OF A DIPROTIC ACID

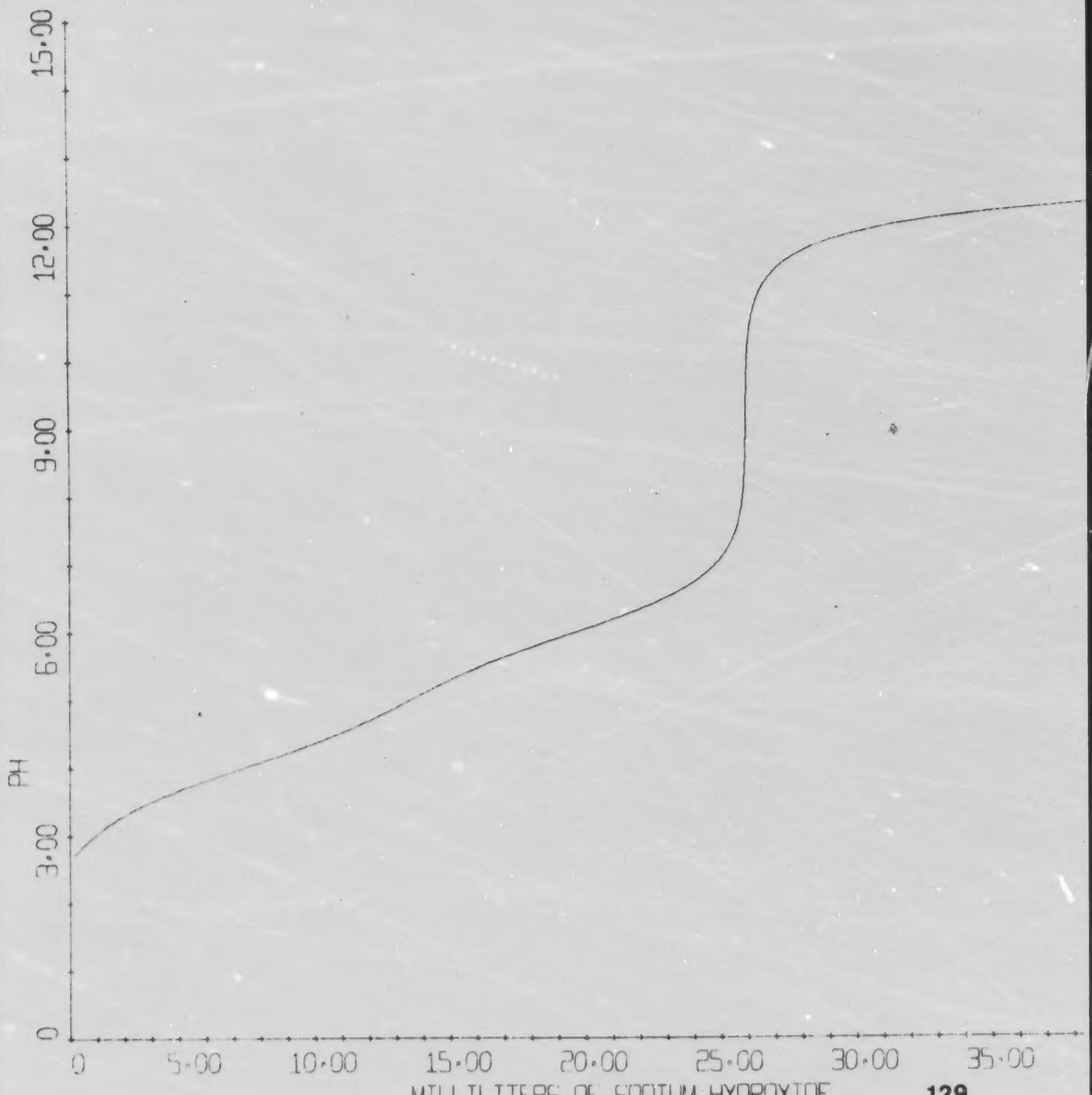
VHA = 25.00
MHA = 0.0500
MMOH = 0.1000
KHHA = 1.E-4
KHA = .25E-4



128

NUMBER OF ENDPOINTS IN THE TITRATION OF A DIPROTIC ACID

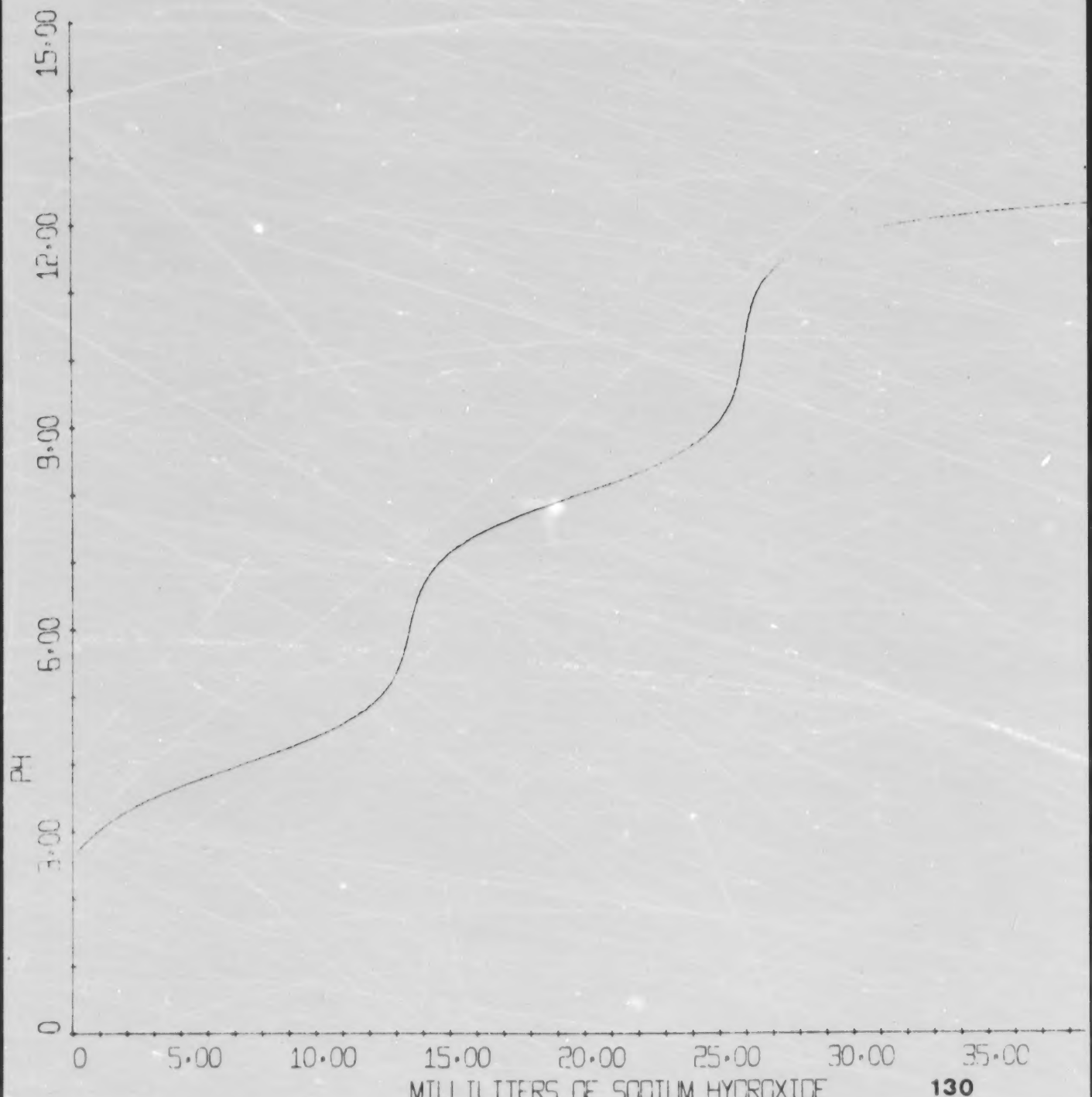
VHA = 25.00
MHA = 0.0500
MMOH = 0.1000
KHHA = 1.E-4
KHA = 1.E-6



129

NUMBER OF ENDPOINTS IN THE TITRATION OF A DIPROTIC ACID

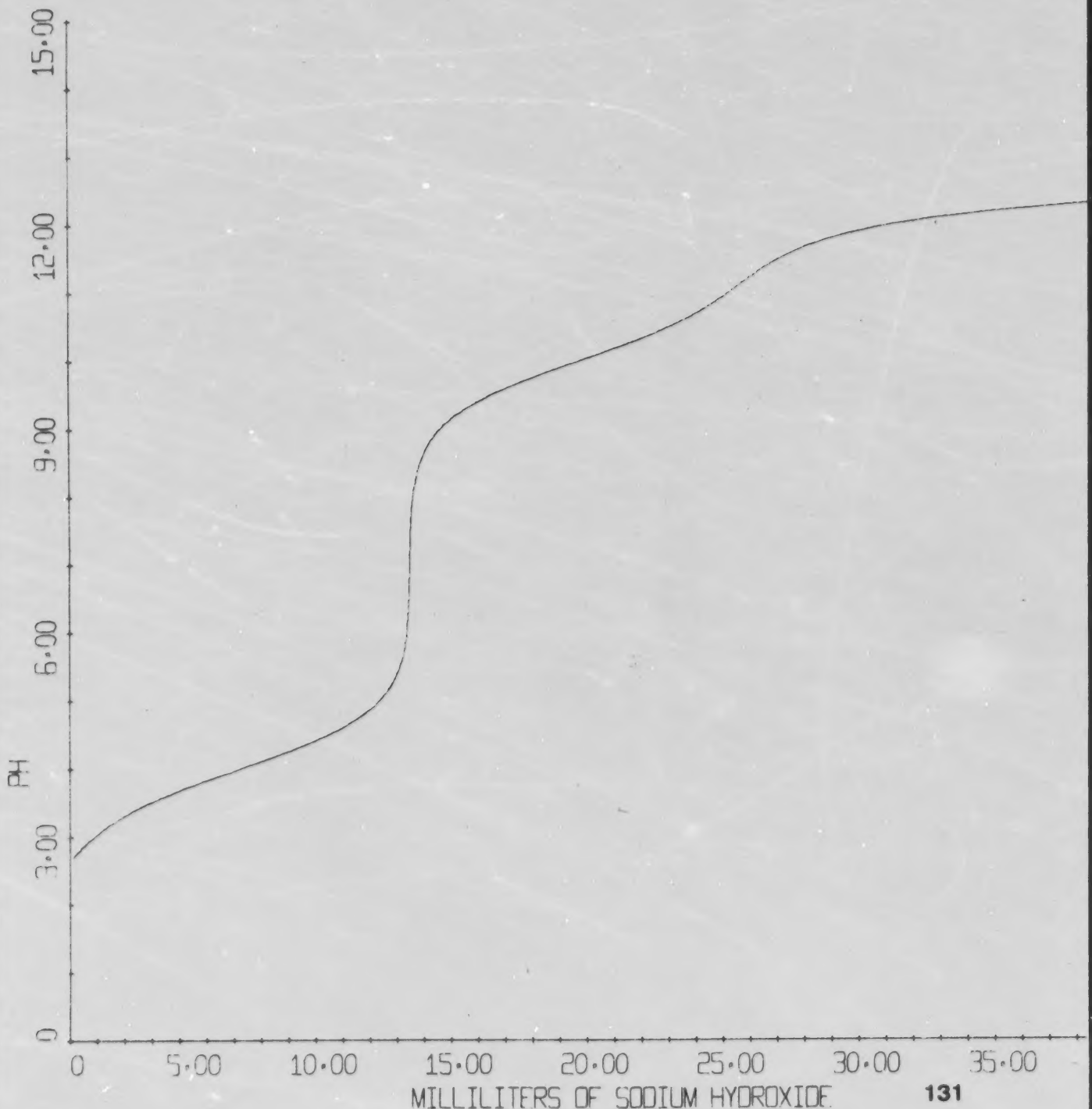
VHA = 25.00
MHA = 0.0500
MMOH = 0.1000
KHHA = 1.E-4
KHA = 1.E-8



130

NUMBER OF ENDPOINTS IN THE TITRATION OF A DIPROTIC ACID

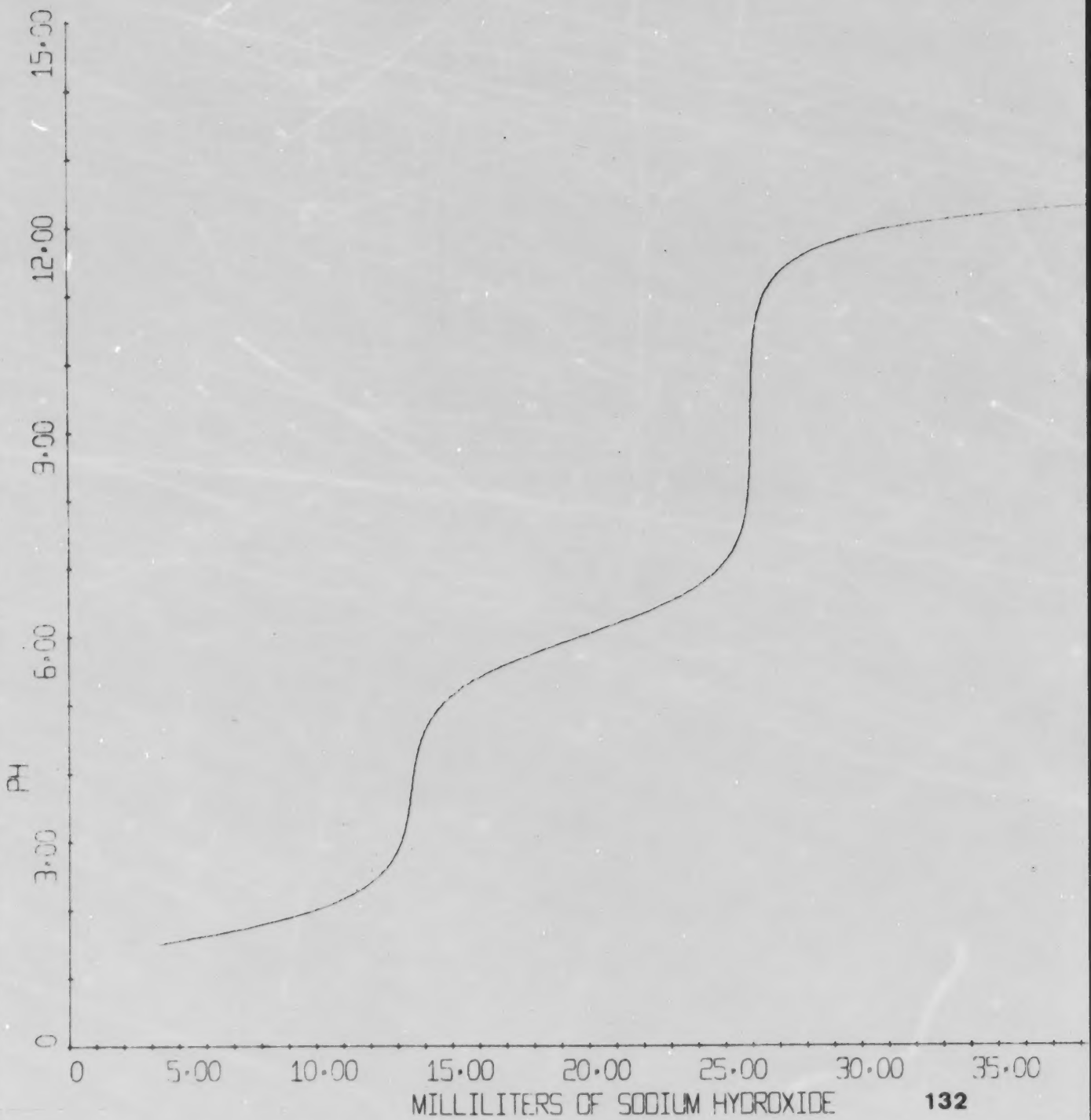
VHA = 25.00
MHA = 0.0500
MMOH = 0.1000
KHHA = 1.E-4
KHA = 1.E-10



131

NUMBER OF ENDPOINTS IN THE TITRATION OF A DIPROTIC ACID

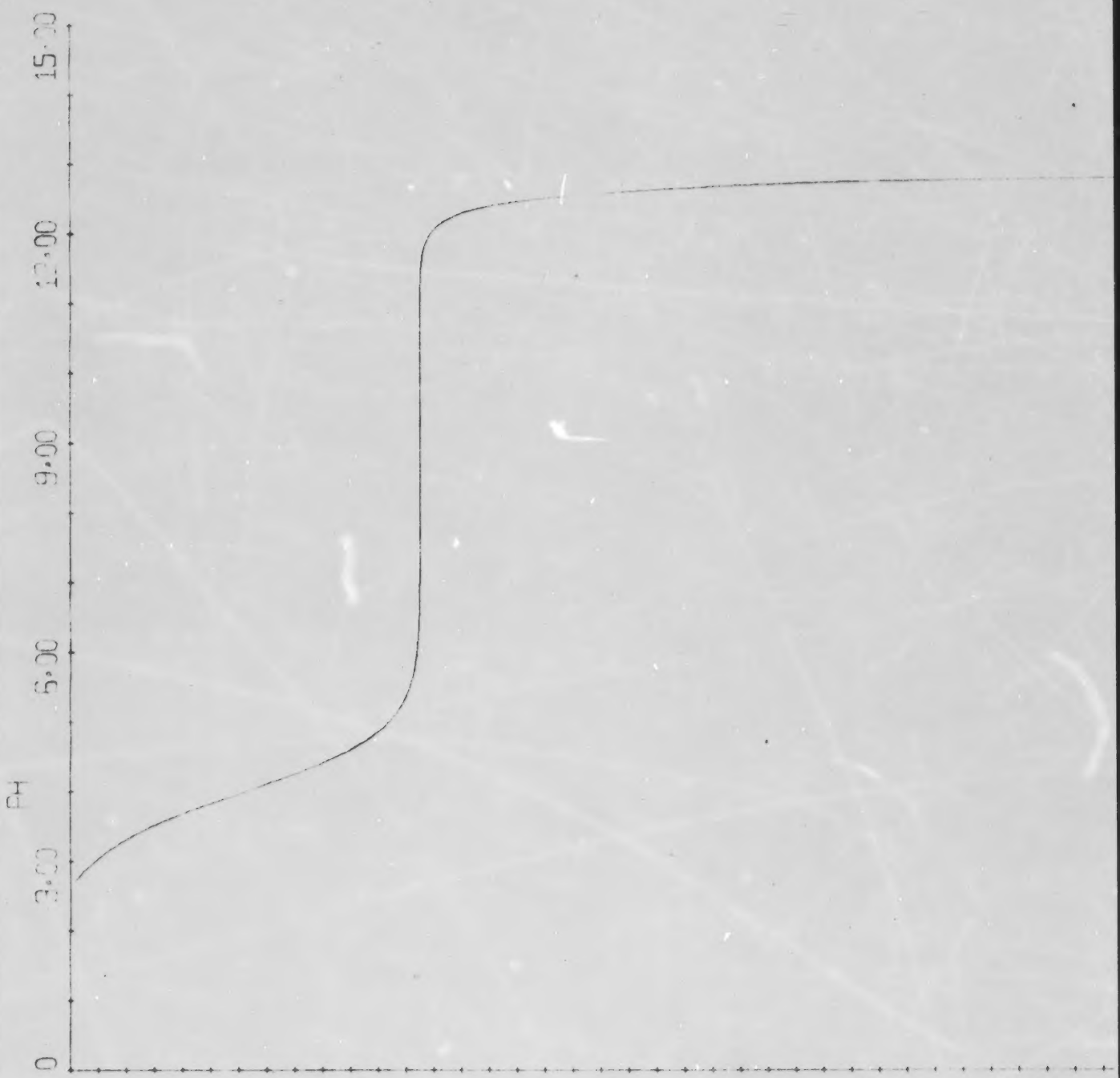
VHA = 25.00
MHA = 0.0500
MMOH = 0.1000
KHHA = 1.
KHA = 1.E-6



132

NUMBER OF ENDPOINTS IN THE TITRATION OF A DIPROTIC ACID

VHA = 25.00
MHA = 0.0500
MMOH = 0.1000
KHHA = 1.E-4
KHA = 1.E-13



133

You can learn a great deal about diprotic acid titrations by studying and comparing and contrasting the graphs presented here, and by trying some different sets of conditions for your own calculations. You probably will find the following special cases helpful in reading some chemistry into the computer simulations.

☑ Case of $K_{H_2A} = 4 \cdot K_{HA^-}$. This is a simulation of the titration of a diprotic carboxylic acid in which the two protons are bound by indistinguishable, non-interacting groups.

For an algebraic discussion of the relationships between macroscopic and microscopic equilibrium constants for such an acid, and the reason for the factor 4, see G. M. Fleck, Equilibria in Solution, New York: Holt, Rinehart and Winston, Inc., 1966, pp. 91 - 93.

A titration curve calculated with such a set of equilibrium constants is presented on page 128. This titration curve has exactly the same shape as the curve for a monoprotic acid present in twice the molar concentration as the diprotic acid. Interpreted as a monoprotic acid, what would be the numerical value of the single equilibrium constant? There is clearly just a single endpoint in the titration of this acid.

☑ Case of $K_{HA^-} < (H^+)_{\text{lowest value in titration}}$. Under these conditions, only a small fraction of the second protons can be removed, and the diprotic acid behaves as if it were a monoprotic acid. The titration curve has the same shape as the corresponding curve for a monoprotic acid of the same concentration. See page 133 for one such case. Interpreted as a monoprotic acid, what would be the numerical value of the single equilibrium constant?

☑ Case of $K_{H_2A} > 10^4 \cdot K_{HA^-}$. This large difference in equilibrium constant values implies that the groups that bind the two protons are chemically very different, or that they are strongly interacting. The titration curve reveals two endpoints if the pH at the conclusion of the titration is high enough. If the value of K_{HA^-} is too small, or if M_{NaOH} is too small, then the removal of the second protons may be supressed, and the second endpoint may not be observed. Compare the titration curves presented on pages 129 — 132.

• *For one of the simulations that yields two endpoints, find a set of numerical values for the four microscopic equilibrium constants that is consistent with the assumed values of the two macroscopic equilibrium constants. Is your set of values for the micro constants the only possible set?*

• *Investigate the effect of concentrations on the existence of two endpoints in the titration of a diprotic acid. Is there any concentration effect? Which (acid or titrant) concentration has the greater effect? Why?*

EXTENDING THE HALF-EQUIVALENCE METHOD TO THE ESTIMATION OF BOTH EQUILIBRIUM CONSTANTS FOR THE DISSOCIATION OF A DIPROTIC ACID

A close look at several computer-simulated titration curves for monoprotic acids showed that the macroscopic half-equivalence method yields reliable values for equilibrium constants within the range $4 < pK < 10$, and values that are useful as estimates for a successive-approximations procedure well outside that range. We were able to gain insight into the method, getting a feeling for both its usefulness and its limitations, by looking at the results of some numerical calculations.

In order to interpret your titration data for a diprotic acid in terms of the chemical and mathematical models presented in this case study, you need a method for making informed guesses of the numerical values of two dissociation constants for that acid. It would be nice indeed if an extension of the half-equivalence method could be used. We shall explore the possibilities, testing the validity of such an extension by making some calculations with the IBM 1130 computer, using FORTRAN Program 11. We shall call this extension *the partial-equivalence point method* of estimating equilibrium constant values by inspection of a titration curve.

USE OF A "DO LOOP" IN A FORTRAN PROGRAM

A new programming feature is introduced in this program. We have used a DO loop that enables us to do the same sequence of operations twice without punching a duplicate set of cards. Had we wanted, the DO loop could have been repeated many times. The statement

11

```
// JOB                S71007,S51


// FOR
* LIST SOURCE PROGRAM
*IOCS(CARD, 1132 PRINTER, TYPEWRITER, PLOTTER)
*ONE WORD INTEGERS

C      TEST OF THE VALIDITY OF THE PARTIAL-EQUIVALENCE METHOD
C      FOR EVALUATING THE EQUILIBRIUM CONSTANTS

C      DIPROTIC ACID

       REAL KHA, KHHA, KW, NUM, MHA, MMOH
       VHA = 25.00
       MHA = 0.0500
       MMOH = 0.1000
       KHHA = 1.E-3
       KHA = 1.E-5
       KW = 1.008E-14
       CALL PREP (.2, .55, 1., 1.)
       WRITE (7,15)
   15  FORMAT ('TEST OF THE HALF-EQUIVALENCE METHOD FOR A DIPROTIC ACID')

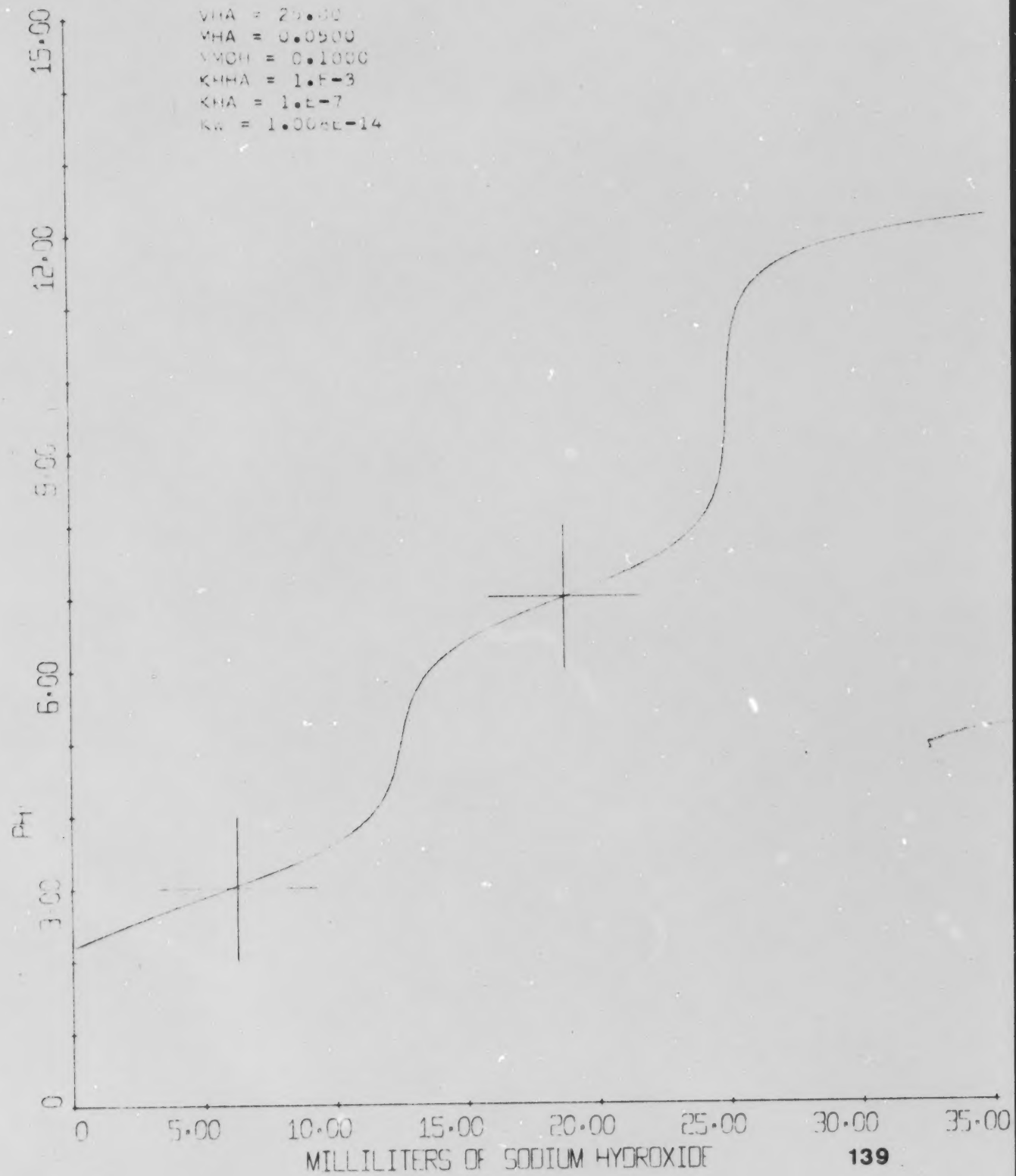
C      MARKING OF THE HALF-EQUIVALENCE VOLUMES
C      MARKING PH = PKHA, AND PH = PKHHA
       VMOH = 1.50*VHA*MHA/MMOH
       PH = -(ALOG(KHA))/2.303
       DO 20 I = 1, 2
       VMOH1 = VMOH - 3.
       VMOH2 = VMOH + 3.
       PH1 = PH - 1.
       PH2 = PH + 1.
       CALL FPLOT(1,VMOH,PH1)
       CALL FPLOT(-2,VMOH,PH1)
       CALL FPLOT(-2,VMOH,PH2)
       CALL FPLOT(1,VMOH1,PH2)
       CALL FPLOT(-2,VMOH1,PH)
       CALL FPLOT(-1,VMOH2,PH)
       VMOH = .50*VHA*MHA/MMOH
   20  PH = -(ALOG(KHHA))/2.303

C      CALCULATION AND PLOTTING OF THE TITRATION CURVE
       H = 1.
    1  H = H - .1*H
       PH = -(ALOG(H))/2.303
       NUM = H**4 + KHHA*(H**3) + (KHHA*KHA - KHHA*MHA - KW)*(H**2)
      *-(2*KHHA*KHA*MHA + KW*KHHA)*H - KW*KHA*KHHA
       DEN = H**4 + (KHHA+MMOH)*(H**3) + (KHHA*KHA + KHHA*MMOH - KW)
      **(H**2) + (KHHA*KHA*MMOH - KW*KHHA)*H - KW*KHHA*KHA
       VMOH = -VHA*NUM/DEN
       IF (VMOH) 1,2,2
    2  CALL FPLOT (-2,VMOH,PH)
    5  H = H - .1*H
       PH = -(ALOG(H))/2.303
```

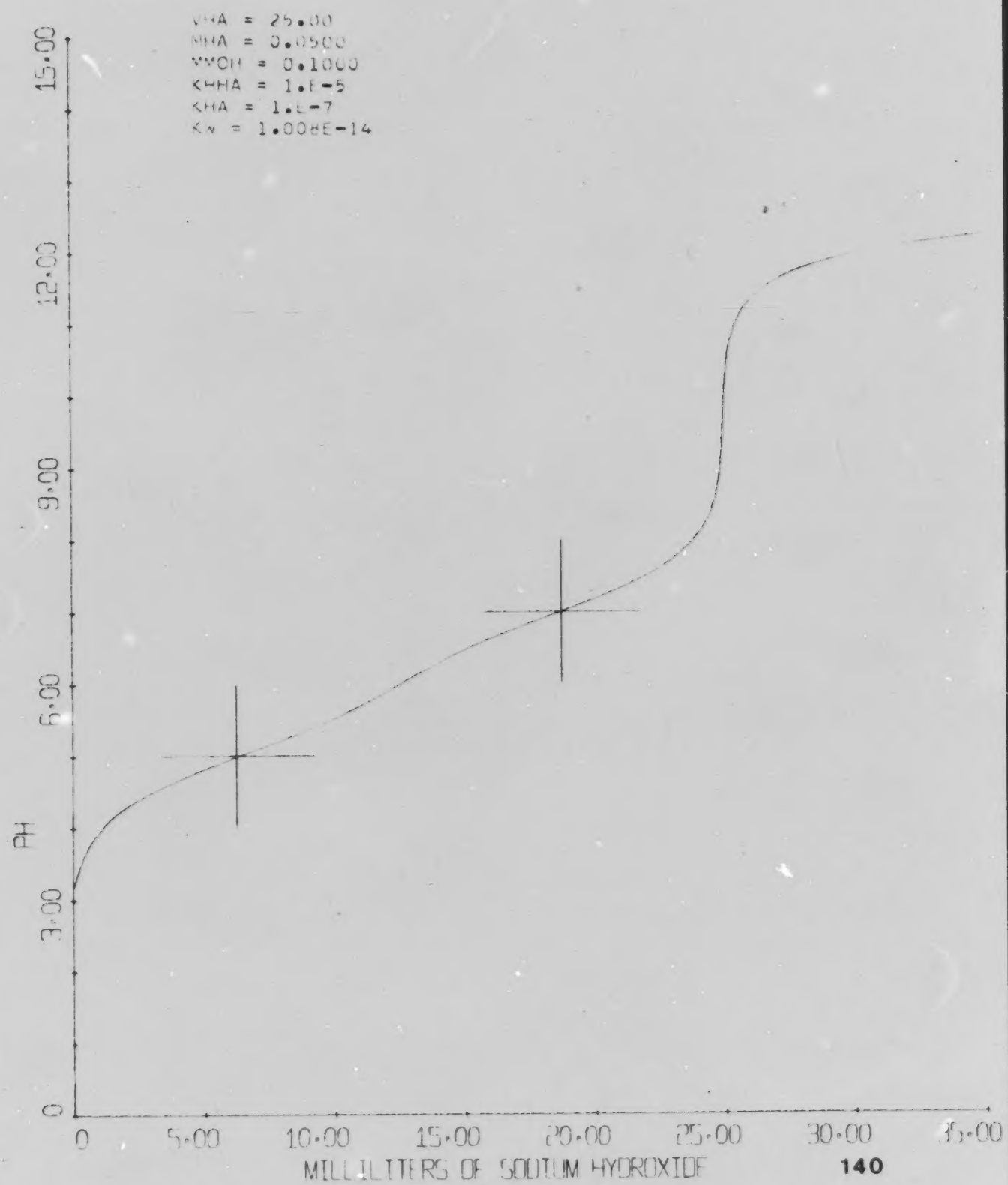
```
      NUM = H**4 + KHHA*(H**3) + (KHHA*KHA - KHHA*MHA - KW)*(H**2)
     *-(2*KHHA*KHA*MHA + KW*KHHA)*H - KW*KHA*KHHA
      DEN = H**4 + (KHHA+MMOH)*(H**3) + (KHHA*KHA + KHHA*MMOH - KW)
     **(H**2) + (KHHA*KHA*MMOH - KW*KHHA)*H - KW*KHHA*KHA
      VMOH = -VHA*NUM/DEN
      IF (35.-VMOH) 10,3,3
    3 CALL FPLOT (0,VMOH,PH)
      GO TO 5
   10 CALL YAXIS (0.,0.,1.,15,5)
      WRITE (7,17)
   17 FORMAT ('PH')
      CALL XAXIS (0., 0., 5., 7, 7)
      WRITE (7,16)
   16 FORMAT ('MILLILITERS OF SODIUM HYDROXIDE')
      CALL FINPL
      CALL EXIT
      END

// XEQ
```

TEST OF THE HALF-EQUIVALENCE METHOD FOR A DIPROTIC ACID

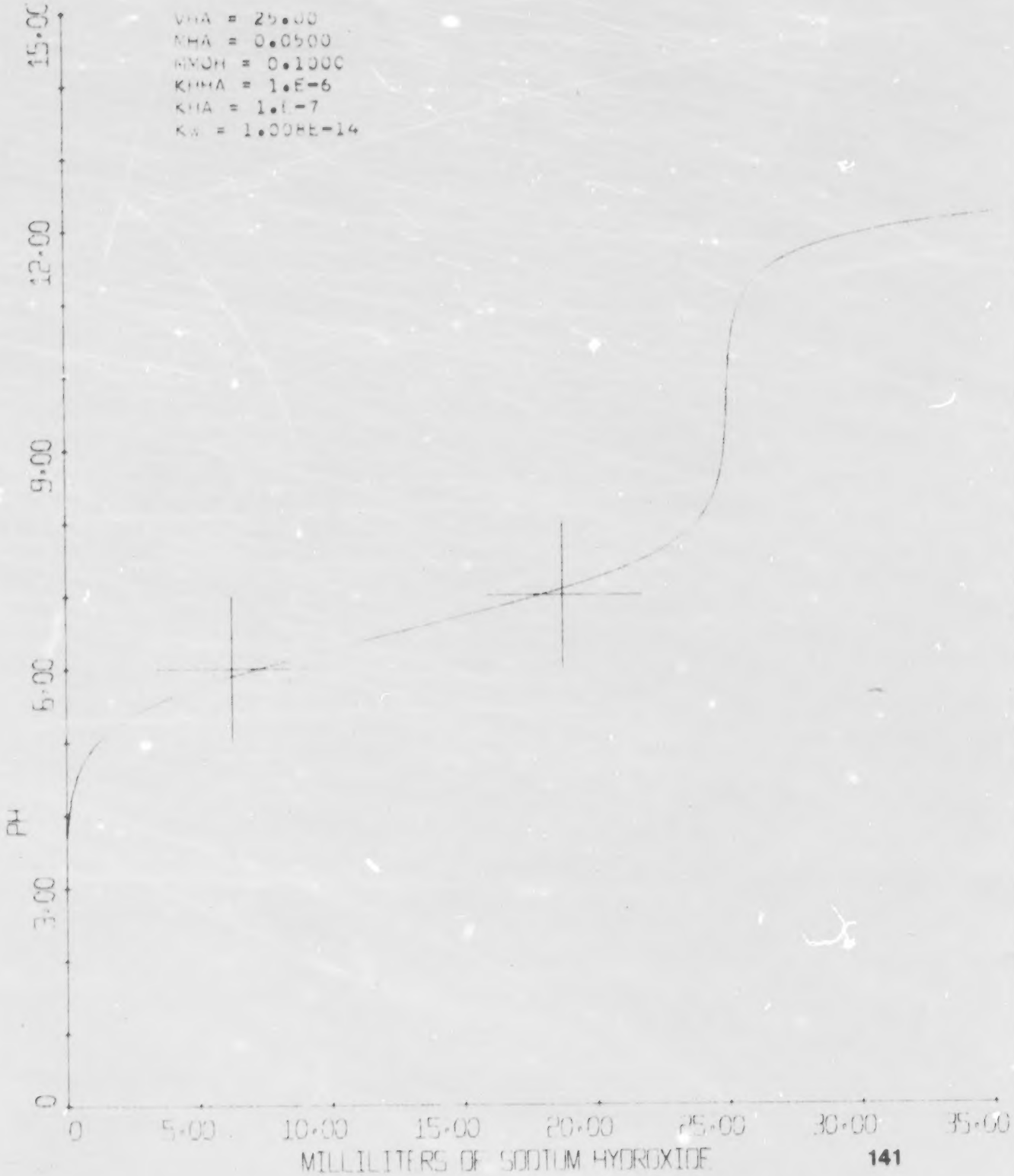


TEST OF THE HALF-EQUIVALENCE METHOD FOR A DIPROTIC ACID



140

TEST OF THE HALF-EQUIVALENCE METHOD FOR A DIPROTIC ACID



141

```
DO 20 I = 1, 2
```

is a command to execute in sequence all the following statements to, and including, statement 20 — and then to return and repeat the entire sequence again. The integer I is a counter which is set initially at 1 and which increases by 1 each time through the DO loop. When the counter gets to 2, then the DO loop is executed for the final time, and the program continues past statement 20.

A more general form of the DO statement is

```
DO N I = J, K
```

where N is a statement number (the number of the terminal statement in the DO loop), J is an integer that gives the initial value of the counter, and K is another integer that specifies the test value of the counter, the value which I may not exceed.

SOME TESTS OF THE VALIDITY OF THE METHOD FOR DIPROTIC ACIDS

We shall define two partial-equivalence points as the points in the titration at which ¼ and ¾ of the final titrant volume have been added to the sample. If all the protons from a particular functional group were removed before any of the protons of the other group in the acid molecule, then the point at which ¼ of the titrant is added would represent the macroscopic half-equivalence point for titration of the first group. Such an extreme situation never is realized, but there is nothing to prevent us from defining these two places in a titration as the first and second partial-equivalence points. The relevant question is: *"Is there a simple relationship between the* pH *values at the partial-equivalence points and the values of the two equilibrium constants for the acid?"* The answer: "Often, yes!"

Inspection of the three titration curves, marked by the computer to show the two partial-equivalence point volumes and the two pH values equal to the pK values, gives us some assurance that this partial-equivalence method does indeed have some validity. On page 140 we see that for a 0.05 molar acid with pK values of 5 and 7, excellent values of the two equilibrium constants can be obtained by direct inspection of the curve: that is, the two crosses have their points of intersection on the titration curve, at least within the limits of the accuracy of the plotter. With pK values of 3 and 7, the second partial-equivalence point cross lies on the curve, although there is some discrepancy with the first; perhaps pK = 3 is too small for the method to work precisely, although clearly this would be adequate for a first guess in a successive-approximations procedure. With pK values of 6 and 7 (page 141), the agreement is not so good, although again the values obtained would be adequate as first guesses for a procedure that could lead to refined values.

Then what can we conclude? It may be dangerous to generalize from these three calculations, but it does appear that:

¶For acids with certain values of the two equilibrium constants, the two pK values are equal to the pH values obtained when one-fourth and three-fourths of the equivalence point volume of titrant have been added.

¶If the values of the two equilibrium constants are very nearly equal (differing only by a factor of 10 or 100), then the method loses accuracy, but the values obtained may be ade-

quate for first guesses in a successive-approximations procedure.

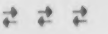
¶If one of the equilibrium constants lies outside the range $4 < pK < 10$, then the method loses accuracy for that equilibrium constant.

• *Perform calculations designed to investigate the effect of acid concentration on the validity of the partial-equivalence method.*

The conclusions presented above are based on the results of just three calculations. Perform calculations designed to test these conclusions. What sort of values of equilibrium constants and concentrations would provide some critical tests?

For the previously-investigated case of a monoprotic acid, the algebra shows that the macroscopic half-equivalence method is rigorously exact only for the single value pK = 7. [G. M. Fleck, Equilibria in Solution, New York: Holt, Rinehart and Winston, Inc., 1966, pp. 68 - 70.] *Is there any situation in which the partial-equivalence method is rigorously exact for a diprotic acid?*

What sections of the titration curve are influenced most by the particular value of K_{H_2A}? *by* K_{HA^-}? *What experimental data need to be most accurate for precise and accurate determination of these equilibrium constants? Design and perform some calculations to substantiate your statements.*



CHANGES IN THE THREE DISTRIBUTION FRACTIONS DURING THE TITRATION OF A DIPROTIC ACID

During the titration of a solution of the diprotic acid H_2A, the relative concentrations of the three species H_2A, HA^-, and $A^=$ change. It is informative to examine in some detail how these concentrations change, because some of the differences between diprotic acids are revealed in the striking differences in the dependence of the species distribution fractions on pH and on V_{NaOH}.

Equations 48, 49, and 51 can be combined in three different ways to yield three distribution-fraction equations:

$$\frac{(HA^-)}{[A]} = \frac{1}{\frac{(H^+)}{K_{H_2A}} + 1 + \frac{K_{HA^-}}{(H^+)}} \tag{56}$$

$$\frac{(H_2A)}{[A]} = \frac{1}{1 + \frac{K_{H_2A}}{(H^+)} + \frac{K_{H_2A}K_{HA^-}}{(H^+)^2}} \tag{57}$$

$$\frac{(A^=)}{[A]} = \frac{1}{\frac{(H^+)^2}{K_{H_2A}K_{HA^-}} + \frac{(H^+)}{K_{HA^-}} + 1} \tag{58}$$

FORTRAN Program 12 uses Equations 56, 57 and 58, together with Equation 55, to calculate the changes in the three distribution fractions that are predicted by our model. Three illustrative examples are presented on pages 149 — 151, and we shall examine each in turn.

If both of the carboxylic groups on the acid H_2A are

12

```
// JOB                    S71007,S51


// FOR
* LIST SOURCE PROGRAM
*IOCS(CARD, 1132 PRINTER, TYPEWRITER, PLOTTER)
*ONE WORD INTEGERS
      REAL NUM, KHA, KHHA, MMOH, KW, MHA
      COMMON V, HH, KHA, KHHA, MMOH, KW, MHA, VHA
C     SUBROUTINE PLOT2
C     CALCULATION AND PLOTTING OF THE DISTRIBUTION FRACTIONS
      CALL PREP (.14, 4., 1., 1.)
      CALL YAXIS (0., 0., .1, 10, 2)
      WRITE (7,37)
   37 FORMAT ('DISTRIBUTION FRACTION')
      CALL XAXIS (0., 0., 1., 50, 10)
      WRITE (7,56)
   56 FORMAT ('MILLILITERS OF SODIUM HYDROXIDE')
      VMOH = V
      H = HH
      FHHA = H*H/(H*H + KHHA*H + KHHA*KHA)
      CALL FPLOT (-2,VMOH,FHHA)
   35 H = H - .1*H
      NUM = H**4 + KHHA*(H**3) + (KHHA*KHA - KHHA*MHA - KW)*(H**2)
     *-(2*KHHA*KHA*MHA + KW*KHHA)*H - KW*KHA*KHHA
      DEN = H**4 + (KHHA+MMOH)*(H**3) + (KHHA*KHA + KHHA*MMOH - KW)
     **(H**2) + (KHHA*KHA*MMOH - KW*KHHA)*H - KW*KHHA*KHA
      VMOH = -VHA*NUM/DEN
      FHHA = H*H/(H*H + KHHA*H + KHHA*KHA)
      IF(50.-VMOH) 30,33,33
   33 CALL FPLOT (0,VMOH,FHHA)
      GO TO 35
   30 VMOH = V
      H = HH
      FHA = KHHA*H/(H*H + KHHA*H + KHHA*KHA)
      CALL FPLOT (1,VMOH,FHA)
      CALL FPLOT (-2,VMOH,FHA)
   45 H = H - .1*H
      NUM = H**4 + KHHA*(H**3) + (KHHA*KHA - KHHA*MHA - KW)*(H**2)
     *-(2*KHHA*KHA*MHA + KW*KHHA)*H - KW*KHA*KHHA
      DEN = H**4 + (KHHA+MMOH)*(H**3) + (KHHA*KHA + KHHA*MMOH - KW)
     **(H**2) + (KHHA*KHA*MMOH - KW*KHHA)*H - KW*KHHA*KHA
      VMOH = -VHA*NUM/DEN
      FHA = KHHA*H/(H*H + KHHA*H + KHHA*KHA)
      IF (50.-VMOH) 40,43,43
   43 CALL FPLOT (0,VMOH,FHA)
      GO TO 45
   40 VMOH = V
      H = HH
      FA = KHHA*KHA/(H*H + KHHA*H + KHHA*KHA)
      CALL FPLOT (1,VMOH,FA)
      CALL FPLOT (-2,VMOH,FA)
   55 H = H - .1*H
      NUM = H**4 + KHHA*(H**3) + (KHHA*KHA - KHHA*MHA - KW)*(H**2)
     *-(2*KHHA*KHA*MHA + KW*KHHA)*H - KW*KHA*KHHA
```

```
      DEN = H**4 + (KHHA+MMOH)*(H**3) + (KHHA*KHA + KHHA*MMOH - KW)
     **(H**2) + (KHHA*KHA*MMOH - KW*KHHA)*H - KW*KHHA*KHA
      VMOH = -VHA*NUM/DEN
      FA = KHHA*KHA/(H*H + KHHA*H + KHHA*KHA)
      IF (50.-VMOH) 50,53,53
   53 CALL FPLOT (0,VMOH,FA)
      GO TO 55
   50 CALL FINPL
      CALL EXIT
      END

// DUP

*STORE       WS  UA  PLOT2

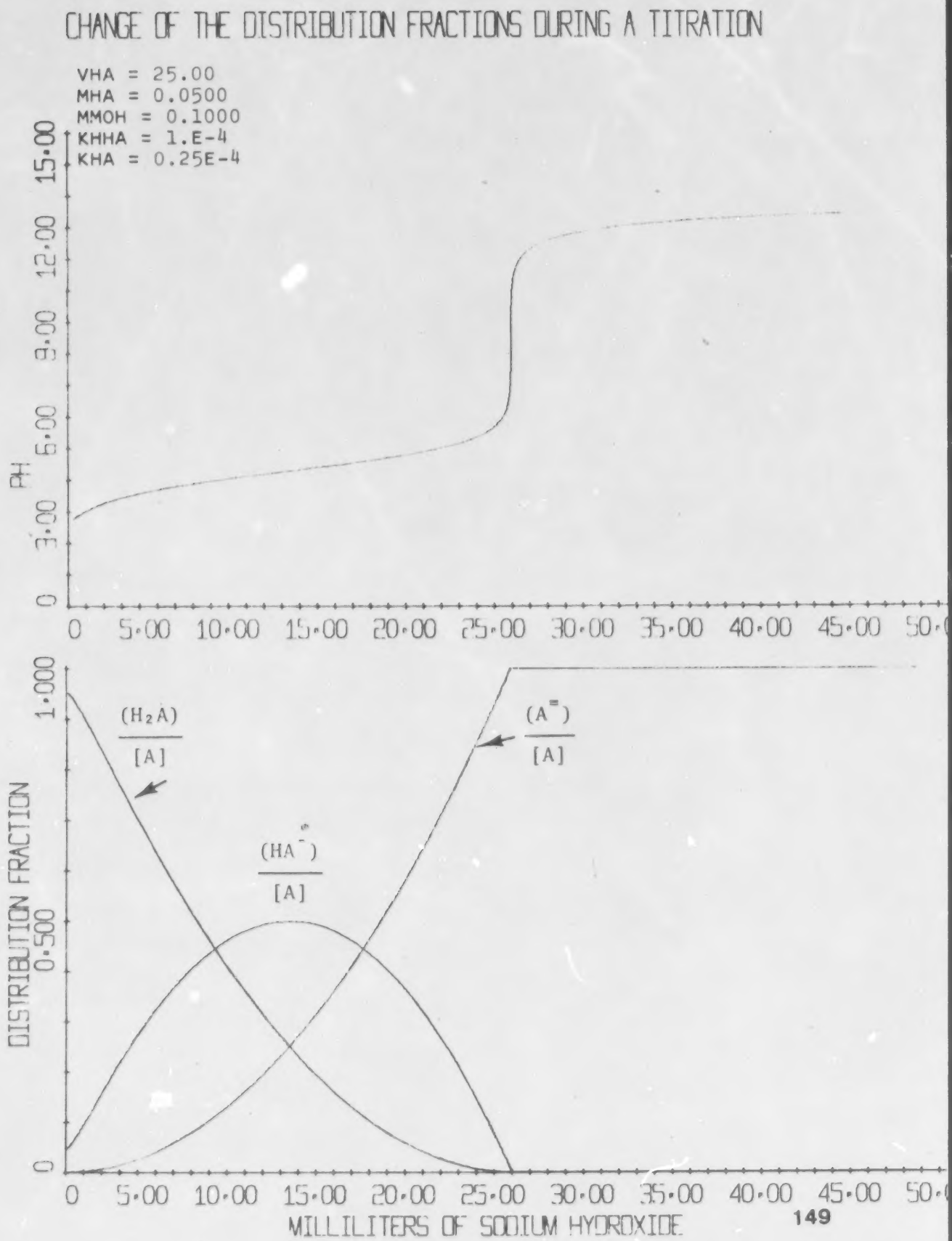

// FOR
*IOCS(CARD, 1132 PRINTER, TYPEWRITER, PLOTTER)
* LIST SOURCE PROGRAM
*ONE WORD INTEGERS
      REAL KHA, KHHA, KW, NUM, MHA, MMOH
      COMMON V, HH, KHA, KHHA, MMOH, KW, MHA, VHA
C     CHANGES IN THE THREE DISTRIBUTION FRACTIONS DURING A TITRATION
      VHA = 25.00
      MHA = 0.0500
      MMOH = 0.1000
      KHHA = 1.E-5
      KHA = 1.E-3
      KW = 1.008E-14
      CALL PREP (.14, .25, 1., 5.5)
      WRITE (7,15)
   15 FORMAT ('CHANGE OF THE DISTRIBUTION FRACTIONS DURING A TITRATION')
      CALL YAXIS (0.,0.,1.,15,5)
      WRITE (7,17)
   17 FORMAT ('PH')
      CALL XAXIS (0.,0.,1.,50,10)

C     CALCULATION OF THE FIRST POINT OF THE TITRATION CURVE
      H = 1.
    1 H = H - .1*H
      PH = -(ALOG(H))/2.303
      NUM = H**4 + KHHA*(H**3) + (KHHA*KHA - KHHA*MHA - KW)*(H**2)
     *-(2*KHHA*KHA*MHA + KW*KHHA)*H - KW*KHA*KHHA
      DEN = H**4 + (KHHA+MMOH)*(H**3) + (KHHA*KHA + KHHA*MMOH - KW)
     **(H**2) + (KHHA*KHA*MMOH - KW*KHHA)*H - KW*KHHA*KHA
      VMOH = -VHA*NUM/DEN
      IF (VMOH) 1,2,2
```

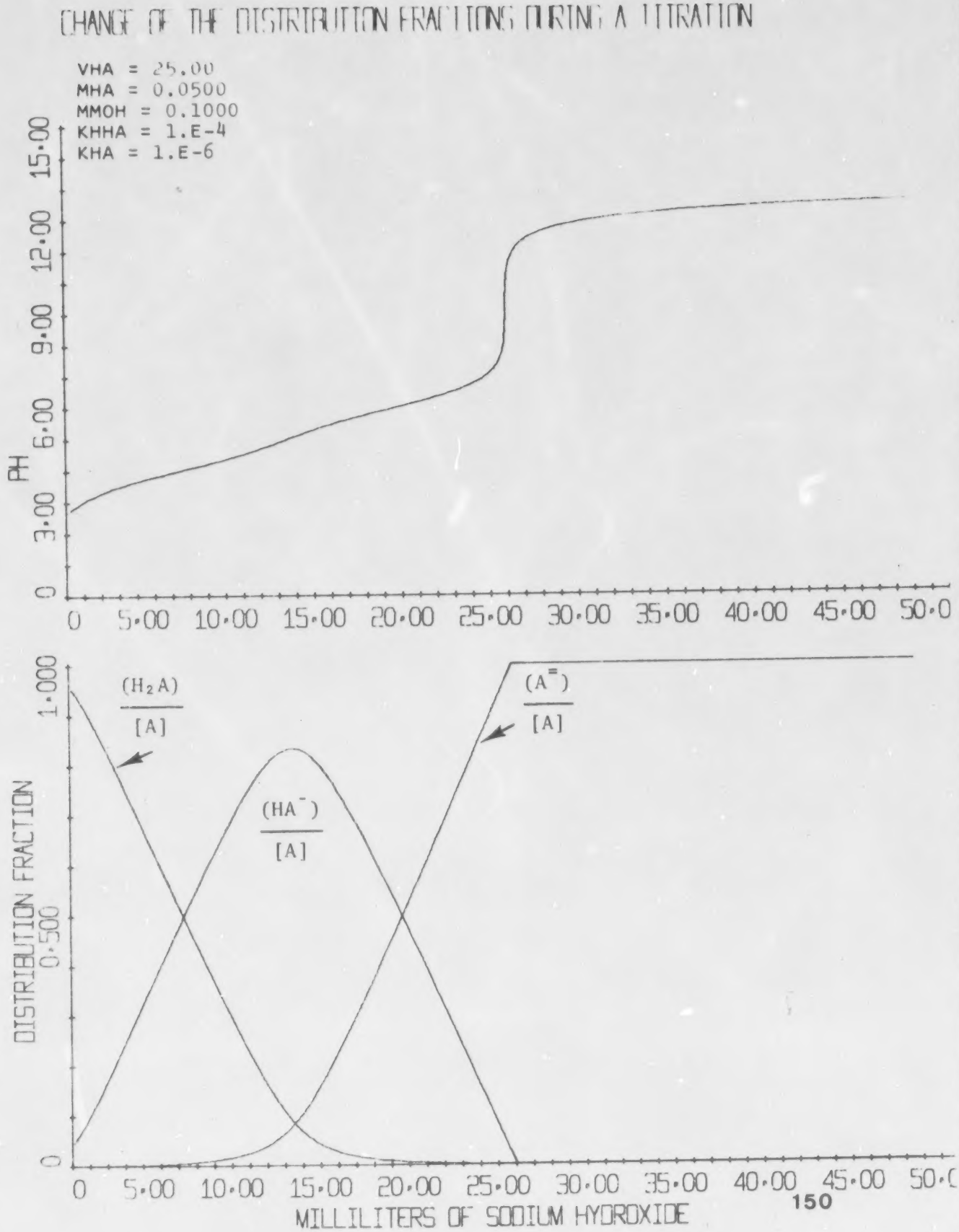
```
      2 CALL FPLOT (-2.,VMOH,PH)
        V = VMOH

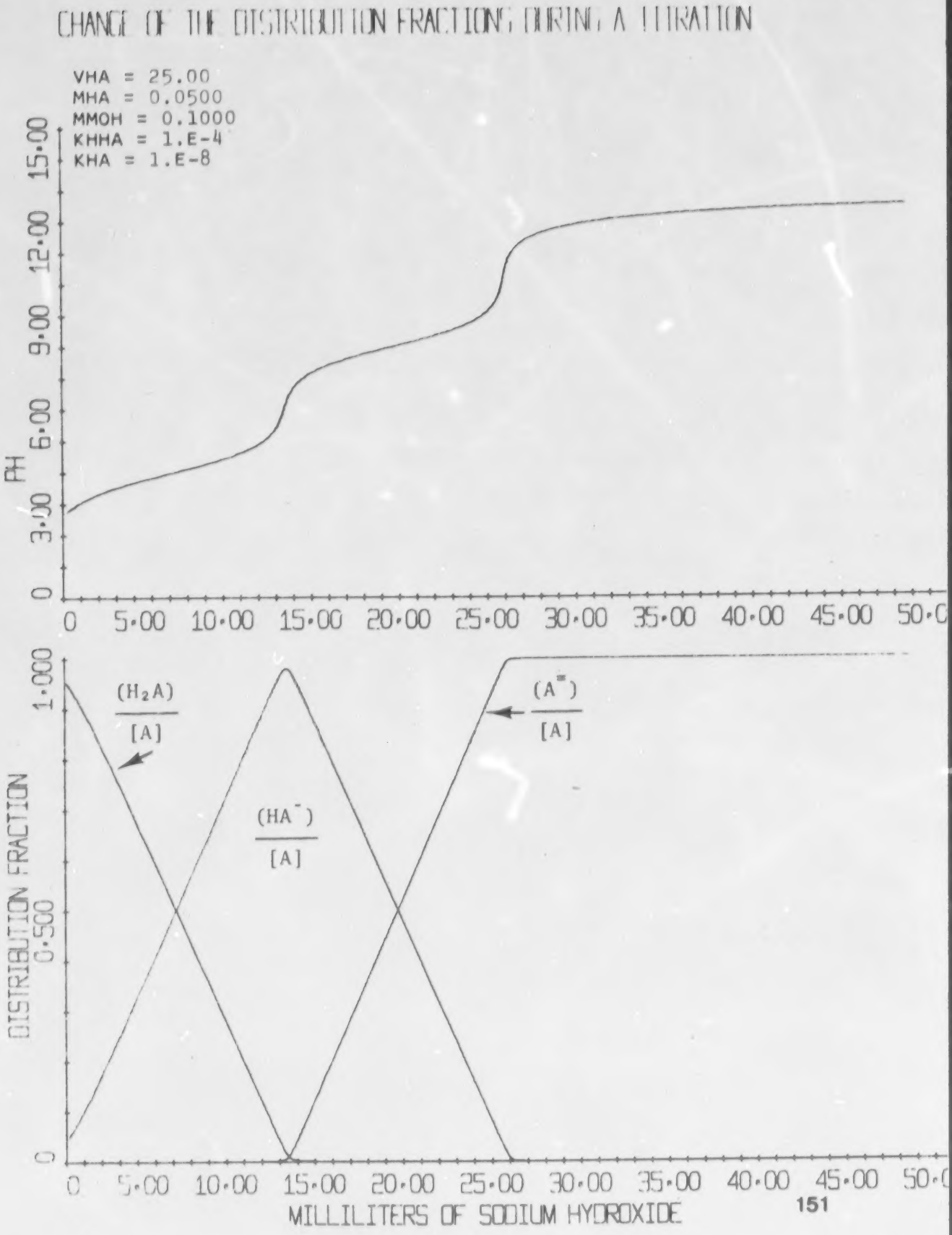
C       CALCULATION AND PLOTTING OF THE TITRATION CURVE
        HH = H
      5 H = H - .1*H
        PH = -(ALOG(H))/2.303
        NUM = H**4 + KHHA*(H**3) + (KHHA*KHA - KHHA*MHA - KW)*(H**2)
       *-(2*KHHA*KHA*MHA + KW*KHHA)*H - KW*KHA*KHHA
        DEN = H**4 + (KHHA+MMOH)*(H**3) + (KHHA*KHA + KHHA*MMOH - KW)
       **(H**2) + (KHHA*KHA*MMOH - KW*KHHA)*H - KW*KHHA*KHA
        VMOH = -VHA*NUM/DEN
        IF(50.-VMOH) 10,3,3
      3 CALL FPLOT (0.,VMOH,PH)
        GO TO 5
     10 CALL FINPL
        CALL LINK(PLOT2)
        END
```

```
// XEQ
```


CHANGE OF THE DISTRIBUTION FRACTIONS DURING A TITRATION
VHA = 25.00
MHA = 0.0500
MMOH = 0.1000
KHHA = 1.E-4
KHA = 0.25E-4
PH
0
3.00
6.00
9.00
12.00
15.00
0
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
50.
DISTRIBUTION FRACTION
0
0.500
1.000
(H2A) / [A]
(HA-) / [A]
(A=) / [A]
MILLILITERS OF SODIUM HYDROXIDE

149


CHANGE OF THE DISTRIBUTION FRACTIONS DURING A TITRATION
VHA = 25.00
MHA = 0.0500
MMOH = 0.1000
KHHA = 1.E-4
KHA = 1.E-6
PH
0
3.00
6.00
9.00
12.00
15.00
0
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
50.0
DISTRIBUTION FRACTION
1.000
0.500
0
(H2A) / [A]
(HA-) / [A]
(A=) / [A]
MILLILITERS OF SODIUM HYDROXIDE


CHANGE OF THE DISTRIBUTION FRACTIONS DURING A TITRATION
VHA = 25.00
MHA = 0.0500
MMOH = 0.1000
KHHA = 1.E-4
KHA = 1.E-8
PH
0
3.00
6.00
9.00
12.00
15.00
0
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
50.0
DISTRIBUTION FRACTION
0
0.500
1.000
(H2A) / [A]
(HA-) / [A]
(A=) / [A]
MILLILITERS OF SODIUM HYDROXIDE

151

identical and noninteracting, then the ratio of the two equilibrium constants is 1:4. All the binding sites for protons are equivalent, and for such a case the protons will distribute themselves in a random, statistically-determined arrangement on the binding sites. At most, only half of the molecules can ever exist as HA^-, and then a fourth are H_2A, and the remaining fourth are $A^=$. This distribution results when there are just half as many protons as sites, so that each site has a probability of $\frac{1}{2}$ of being occupied and a probability of $\frac{1}{2}$ of being empty. The graph on page 149 shows this anticipated distribution at the macroscopic half-equivalence point, where the distribution fraction $(HA^-)/[A]$ reaches its maximum value of $\frac{1}{2}$, and the other two distribution fractions are equal to $\frac{1}{4}$.

• *Perform some calculations to investigate the shapes of the distribution-fraction curves for other sets of two equilibrium constants that stand in the ratio 1:4. The prediction, based on statistical considerations, is that a ratio of 1:2:1 must result when there are just half enough protons to occupy all the binding sites. Does this condition necessarily occur at the macroscopic half-equivalence point? Can you find a situation in which the fraction $(HA^-)/[A]$ does not pass through a maximum of $\frac{1}{2}$?*

In order to achieve a solution in which more than half of the A-containing species are present as HA^-, we must chose an acid that has equilibrium constants that differ by more than a factor of four. Even when the two equilibrium constants differ by a factor of 100 (as is the case depicted on page 150), there

remain significant amounts of species H_2A and $A^{=}$ at the point in the titration where the fraction present as HA passes through its maximum value.

• *Inspection of the graphs on pages 149 — 151 suggests that the fractions* $(H_2A)/[A]$ and $(A^{=})/[A]$ <u>are equal</u> *whenever the fraction* $(HA^{-})/[A]$ *reaches its maximum value. Are there any conditions under which this may not be true?*

• *Under what conditions can solutions be prepared in which two species have distribution fractions each equal to* $\frac{1}{2}$*? Check your answer with appropriate simulations.*

Two endpoints are seen in the titration curve presented on page 151 for a diprotic acid whose equilibrium constants differ by a factor of 10^4. The condition for a sharp endpoint is generally that a few drops of titrant must change the qualitative nature of the chemical solution, and such is the case in this titration. In the vicinity of 12.5 mℓ of added sodium hydroxide solution, the solution changes from a mixture of H_2A and HA^{-} to a mixture of HA^{-} and $A^{=}$. There is essentially no place in the titration where all three species coexist. At 12.5 mℓ, the fraction $(HA^{-})/[A]$ is essentially equal to 1.0, and we can say that at this point all the H_2A has been titrated to HA^{-}; the corresponding statement is not valid for the acids whose titrations are simulated on pages 149 and 150. Likewise, we can speak of a solution of HA^{-} for this acid, but not for the other cases.

• *Write and execute a computer program that gives a numerical output of distribution-fraction values during a titration. By how much do the equilibrium constant values have to differ*

in order that the fraction $(HA^-)/[A]$ can reach the value 0.9? the value 0.95? the value 0.99? the value 0.999? Is the limit equal to exactly 1, or are there restrictions that keep the maximum attainable value of this intermediate species concentration less than 1?

• Which of the various hypothetical cases of diprotic acids presented here correspond to real acids? What, in fact, are the ratios of equilibrium constants that are encountered in the laboratory with common diprotic carboxylic acids? other diprotic acids? Look up some equilibrium-constant values in the library to get a feeling for the range of equilibrium-constant values that can be reasonably expected.

CHANGES IN THE FOUR MICROSCOPIC-SPECIES DISTRIBUTION FRACTIONS DURING THE TITRATION OF A DIPROTIC ACID

When talking about the equilibria involving a diprotic acid, it is often helpful to consider independently the two different species that have the overall composition and charge indicated by the symbol HA^-. Here we explicitly recognize the two species $H\sim A^-$ and $^-A\sim H$ which differ because a different proton binding site is occupied. There is only one species with the formula H_2A, and that is $H\sim A\sim H$. There is also only one species devoid of dissociable protons, and that is $A^=$.

The fully-protonated species can react to form the completely-dissociated species by either of two distinct reaction pathways which differ in the order in which the two protons are removed. The four chemical steps and the associated *microscopic equilibrium constants* in this model for diprotic-acid equilibria are

$$H\sim A\sim H \rightleftarrows H^+ + {}^-A\sim H \qquad K_1 = \frac{(H^+)\langle {}^-A\sim H\rangle}{\langle H\sim A\sim H\rangle} \tag{59}$$

$$H\sim A\sim H \rightleftarrows H^+ + H\sim A^- \qquad K_2 = \frac{(H^+)\langle H\sim A^-\rangle}{\langle H\sim A\sim H\rangle} \tag{60}$$

$$H\sim A^- \rightleftarrows H^+ + A^= \qquad K_3 = \frac{(H^+)\langle A^=\rangle}{\langle H\sim A^-\rangle} \tag{61}$$

$$^-A\sim H \rightleftarrows H^+ + A^= \qquad K_4 = \frac{(H^+)\langle A^=\rangle}{\langle {}^-A\sim H\rangle} \tag{62}$$

where the individual species are written with indication of the position of a bound proton: left and right sides of the letter A indicate different positions in the molecule. The molar con-

centrations of these individual species (we shall call these concentrations *microscopic-species concentrations* whenever there is a need to make a careful distinction) are indicated by enclosing the formula by the symbols ⟨ ⟩. In this section we shall indicate microscopic equilibrium constants by using subscript numbers, and macroscopic equilibrium constants by using subscript formulas.

The four microscopic equilibrium constants K_1, K_2, K_3, and K_4 are not independent. If the numerical values of any three of these K's are known, the value of the fourth can be calculated without difficulty.

• *Combine Equations 59 — 62 to obtain the relationship*

$$K_1K_4 = K_2K_3 \tag{63}$$

However, there are three independent microscopic equilibrium constants, even though there are only two macroscopic equilibrium constants whose values can be obtained by analysis of titration data. This fact implies that knowledge of the values of the experimentally-determined macroscopic equilibrium constants is not sufficient to specify a unique set of values for the four microscopic equilibrium constants. We can, however, obtain some relationships between the macro and micro constants, and we shall proceed with that task at this time.

The link between the macro and micro descriptions of these equilibria is the set of equations

$$(H_2A) = \langle H{\sim}A{\sim}H \rangle \tag{64}$$

$$(HA^-) = \langle {}^-A{\sim}H \rangle + \langle H{\sim}A^- \rangle \tag{65}$$

$$(A^=) = \langle A^= \rangle \tag{66}$$

• *Combine Equations 48, 49, 59 — 62, and 64 — 66 to get the following two relationships between the macroscopic equilibrium constants and the microscopic equilibrium constants:*

$$K_{H_2A} = K_1 + K_2 \tag{67}$$

$$K_{HA^-} = \frac{K_3K_4}{K_3 + K_4} \tag{68}$$

To obtain algebraic equations relating distribution fractions for the four microscopic species to (H^+), we need the conservation equation

$$[A] = \langle H\sim A\sim H\rangle + \langle {}^-A\sim H\rangle + \langle H\sim A^-\rangle + \langle A^{=}\rangle \tag{69}$$

Equations 59 — 62 can be used to eliminate all but one of the microscopic species concentrations in Equation 69. Depending on which concentration remains, we can get any one of four distinct equations which can in turn be rearranged into a consistent form so that the four distribution fractions can be written as

$$\frac{\langle H\sim A\sim H\rangle}{[A]} = \frac{(H^+)^2}{denominator} \tag{70}$$

$$\frac{\langle {}^-A\sim H\rangle}{[A]} = \frac{(H^+)K_2}{denominator} \tag{71}$$

$$\frac{\langle H\sim A^-\rangle}{[A]} = \frac{(H^+)K_1}{denominator} \tag{72}$$

$$\frac{\langle A^{=}\rangle}{[A]} = \frac{K_2K_3}{denominator} \tag{73}$$

where

$$denominator = (H^+)^2 + \{K_1 + K_2\}(H^+) + K_2K_3$$

• *Perform the algebra required to obtain Equations 70 — 73. You may find it convenient or necessary to use Equation 63 to simplify certain expressions.*

• *Show that Equations 56 — 58 can be written as three fractions with a common denominator.*

• *Starting with Equations 70 — 73, and using relationships between microscopic and macroscopic quantities, obtain Equations 56 — 58.*

• *Verify that the four microscopic distribution fractions together add to unity (that is, that the sum of the four fractions is equal to 1).*

COMPUTER CALCULATIONS OF THE MICROSCOPIC DISTRIBUTION FRACTIONS DURING A SIMULATED DIPROTIC ACID TITRATION

FORTRAN Program 13 provides a convenient way to learn about changes in the four microscopic distribution fractions during the course of a titration. The numerical values of three microscopic equilibrium constants are assumed, as well as a set of initial conditions (volume of acid solution and concentrations of acid and base). For the information of the chemist who is using this program to simulate various titrations, there is a printout of pK values for both the microscopic and macroscopic equilibrium constants. Then the program produces a huge array of numbers, a sampling of which is presented on page 160. Actually, you probably cannot find any real acid that behaves like this simulation, since K_3 was assumed to have a larger value than either K_1 or K_2. Generally it is harder to remove the second proton, which means that the second equilibrium constant is smaller.

13

```
// JOB                  S71007,S51
// FOR
* LIST SOURCE PROGRAM
*IOCS(CARD, 1132 PRINTER)
      REAL NUM, KHA, KHHA, KW, MMOH, MHA, K1, K2, K3, K4
C     CALCULATION OF FRACTIONS OF TOTAL A-CONTAINING SPECIES PRESENT
C     AS EACH OF THE MICROSCOPIC SPECIES DURING THE
C     TITRATION OF THE ACID H2A
      K1 = 1.00E-4
      K2 = 3.0E-4
      K3 = 9.0E-4
      K4 = K2*K3/K1
      KHHA = K1 + K2
      KHA = K3*K4/(K3 + K4)
      PK1 = -(ALOG(K1))/2.303
      PK2 = -(ALOG(K2))/2.303
      PK3 = -(ALOG(K3))/2.303
      PK4 = -(ALOG(K4))/2.303
      PKHHA = -(ALOG(KHHA))/2.303
      PKHA = -(ALOG(KHA))/2.303
      WRITE (3,11) PK1, PK2, PK3, PK4
   11 FORMAT('1PK1 =', F6.2, '     PK2 =', F6.2, '     PK3 =', F6.2,
     *'PK4 =', F6.2)
      WRITE (3, 14) PKHHA, PKHA
   14 FORMAT ('1PKHHA =', F6.2, '     PKHA =', F6.2//)
      WRITE (3, 15)
   15 FORMAT ('     (H2A)      (HA)      (AH)      (A)      VMOH      PH')
      VHA = 25.00
      MHA = 0.0500
      MMOH = 0.1000
      KW = 1.008E-14

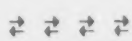
      H = 1.
    1 H = .8*H
      PH = -(ALOG(H))/2.303
      NUM = H**4 + KHHA*(H**3) + (KHHA*KHA - KHHA*MHA - KW)*(H**2)
     *-(2*KHHA*KHA*MHA + KW*KHHA)*H - KW*KHA*KHHA
      DEN = H**4 + (KHHA + MMOH)*(H**3) + (KHHA*KHA + KHHA*MMOH - KW)
     **(H**2) + (KHHA*KHA*MMOH - KW*KHHA)*H - KW*KHA*KHHA
      VMOH = -VHA*NUM/DEN
      IF (VMOH) 2, 20, 20
    2 IF (PH - 7.00) 1, 1, 30
   20 CONTINUE
      FDEN = H**2 + (K1 + K2)*H + K3*K2
      FHAH = (H**2)/FDEN
      FHA = H*K2/FDEN
      FAH = H*K1/FDEN
      FA = K2*K3/FDEN
      PH = -(ALOG(H))/2.303
      WRITE (3,16) FHAH, FHA, FAH, FA, VMOH, PH
   16 FORMAT (6F10.6)
      GO TO 1
   30 CALL EXIT
      END
// XEQ
```

(H2A)	(HA)	(AH)	(A)	VNOH	PH
0.911734	0.257920	0.091558	0.011038	0.007979	2.302422
0.889049	0.070599	0.023533	0.010818	0.628890	2.422315
0.860653	0.085410	0.028476	0.025439	1.265996	2.919207
0.825337	0.102406	0.034135	0.038118	1.896706	3.413106
0.781884	0.121267	0.040422	0.056424	2.892241	2.712993
0.729260	0.141382	0.047127	0.082230	3.993993	2.809865
0.666976	0.161634	0.053878	0.117511	5.257119	2.906778
0.595526	0.180399	0.060133	0.163941	6.790356	3.003670
0.516792	0.195686	0.065228	0.222292	8.522915	3.100563
0.434181	0.205506	0.068502	0.291809	10.495376	3.197455
0.352235	0.208399	0.069466	0.369895	12.530477	3.294346
0.275715	0.203908	0.067969	0.452407	14.548225	3.391241
0.208488	0.192737	0.064245	0.534528	16.441021	3.488133
0.152747	0.176509	0.058836	0.611905	18.127510	3.585026
0.108869	0.157257	0.052419	0.681453	19.564746	3.681919
0.075828	0.136913	0.045637	0.741620	20.746391	3.778811
0.051937	0.116996	0.038998	0.792167	21.692054	3.875704
0.034917	0.098508	0.032836	0.833738	22.434822	3.972596
0.023250	0.081991	0.027330	0.867428	23.011386	4.069489
0.015343	0.067638	0.022546	0.894472	23.456131	4.166381
0.010057	0.055416	0.018472	0.916054	23.797408	4.263275
0.006557	0.045163	0.015054	0.933224	24.061981	4.360167
0.004257	0.036659	0.012219	0.946863	24.269407	4.457059
0.002756	0.029662	0.009887	0.957693	24.422943	4.553952
0.001779	0.023943	0.007981	0.966295	24.542406	4.650845
0.001147	0.019290	0.006430	0.973132	24.640965	4.747737
0.000738	0.015518	0.005172	0.978570	24.715812	4.844630
0.000474	0.012469	0.004156	0.982899	24.774627	4.941522
0.000304	0.010010	0.003336	0.986347	24.820991	5.038415
0.000195	0.008030	0.002675	0.989096	24.857624	5.135308
0.000125	0.006438	0.002146	0.991289	24.886634	5.232200
0.000080	0.005160	0.001720	0.993039	24.909656	5.329092
0.000051	0.004134	0.001378	0.994436	24.927945	5.425986
0.000033	0.003310	0.001103	0.995552	24.942504	5.522878
0.000021	0.002651	0.000883	0.996444	24.954097	5.619771
0.000013	0.002122	0.000707	0.997156	24.963333	5.716663
0.000008	0.001698	0.000565	0.997726	24.970710	5.813556
0.000005	0.001359	0.000453	0.998181	24.976589	5.910449
0.000003	0.001088	0.000362	0.998545	24.981288	6.007341
0.000002	0.000870	0.000290	0.998836	24.985042	6.104233
0.000001	0.000696	0.000232	0.999069	24.988044	6.201127
0.000000	0.000557	0.000185	0.999255	24.990444	6.298019
0.000000	0.000446	0.000148	0.999404	24.992366	6.394911
0.000000	0.000356	0.000118	0.999523	24.993892	6.491804
0.000000	0.000285	0.000095	0.999619	24.995113	6.588697
0.000000	0.000228	0.000076	0.999695	24.996111	6.685589
0.000000	0.000182	0.000060	0.999756	24.996900	6.782482
0.000000	0.000146	0.000048	0.999804	24.997535	6.879374
0.000000	0.000116	0.000038	0.999844	24.998040	6.976267
0.000000	0.000093	0.000031	0.999875	24.998462	7.073160
0.000000	0.000074	0.000024	0.999900	24.998795	7.170052
0.000000	0.000059	0.000019	0.999920	24.999069	7.266945
0.000000	0.000047	0.000015	0.999936	24.999298	7.363838
0.000000	0.000038	0.000012	0.999948	24.999485	7.460730
0.000000	0.000030	0.000010	0.999959	24.999636	7.557622
0.000000	0.000024	0.000008	0.999967	24.999805	7.654516
0.000000	0.000019	0.000006	0.999974	24.999850	7.751408
0.000000	0.000015	0.000005	0.999979	25.000021	7.848300
0.000000	0.000012	0.000004	0.999983	25.000242	7.945193
0.000000	0.000010	0.000003	0.999986	25.000385	8.042087
0.000000	0.000008	0.000002	0.999989	25.000556	8.138978

This program calculates pairs $\{V_{NaOH}, pH\}$ for a titration, and then uses the pH value (actually, it uses the value of the concentration of H^+) together with Equations 70 — 73 to calculate values of FHAH, FHA, FAH and FA, the four microscopic distribution fractions, at each pH value. Statement 20 has not been used in previous programs; it doesn't do anything, but it seemed to be a good place to branch for an IF statement. The CONTINUE statement could have been eliminated by numbering the following statement as № 20.

One significant feature of the data from this simulation should be noted. The ratio $\langle H\sim A^- \rangle / \langle {}^-A\sim H \rangle$ is constant throughout the titration. Since this ratio does not depend on pH, there is no information about the ratio that can be obtained from the shape of a titration curve. There is in fact information about <u>just two</u> equilibrium constants in the titration data. This fact means that analysis of a titration curve yields insufficient data for evaluation of the microscopic equilibrium constants.

Chemists can and have evaluated the microscopic equilibrium constants for diprotic acids, often by very clever means. For a discussion of the evaluation of micro constants for amino acids, see J. T. Edsall, "Dipolar Ions and Acid-Base Equilibria," chap. 4 in E. J. Cohn and J. T. Edsall, <u>Proteins, Amino Acids and Peptides</u> (American Chemical Society Monograph № 90), New York: Reinhold Publishing Corp., 1943.



CONFRONTATION OF EXPERIMENTAL DATA WITH THE PREDICTIONS OF A DIPROTIC-ACID MODEL: A STRATEGY FOR EVALUATING TWO EQUILIBRIUM CONSTANTS

The critical test of a chemical model is a confrontation of the predictions of that model with data from appropriately designed experiments. Such a confrontation simultaneously tests both the adequacy of the model to interpret the data, and the adequacy of the data to test the model. With our model, we use the process of confronting data and model to find the set of two macroscopic equilibrium constants that bring data and model into the best quantitative agreement. The result is that we can obtain numerical values for the two equilibrium constants. We are attempting to obtain a consistent description of the chemistry of a diprotic acid in solution.

The shape of the titration curve is most sensitive to the numerical value of K_{H_2A} in the vicinity of the first partial-equivalence point (that is, near the point where the volume of added titrant is ¼ of the volume required to reach the equivalence point of the titration). These are the data that are most useful in evaluating that equilibrium constant. The numerical predictions of the model are most sensitive to the numerical value of K_{HA^-} in the vicinity of the second partial-equivalence point (near the point where ¾ of the equivalence-point volume of titrant has been added), and these data are the most useful in evaluating that equilibrium constant. *Only a few carefully-selected numbers from your experimental titration data are needed for the successive-approximations procedure that leads to*

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// JOB                    S71007,S51

// FOR
* LIST SOURCE PROGRAM
*IOCS(CARD, 1132 PRINTER)
C       CONFRONTATION OF THE DATA WITH PREDICTIONS FOR A DIPROTIC ACID
        REAL KHA, KHHA, KW, NUM, MHA, MMOH
        VHA = 25.00
        MHA = 0.05
        MMOH = 0.10
        KHHA = .9E-6
        KHA = 1.1E-7
        KW = 1.E-14
     28 READ (2,25) V, PH
     25 FORMAT (F20.2, F20.2)
        IF (V) 30,29,29
     29 H = 10**(-PH)
        NUM = H**4 + KHHA*(H**3) + (KHHA*KHA - KHHA*MHA - KW)*(H**2)
       *-(2*KHHA*KHA*MHA + KW*KHHA)*H - KW*KHA*KHHA
        DEN = H**4 + (KHHA + MMOH)*(H**3) + (KHHA*KHA + KHHA*MMOH - KW)
       **(H**2) + (KHHA*KHA*MMOH - KW*KHHA)*H - KW*KHA*KHHA
        VMOH = -VHA*NUM/DEN
        WRITE (3,10) PH, VMOH, V
     10 FORMAT (3F7.2)
        GO TO 28
     30 CALL EXIT
        END
// XEQ

   5.03    1.14    1.25
   5.32    2.09    2.28
   5.71    4.36    4.65
```

numerical values for the two equilibrium constants for the acid. Then the full set of data from throughout the titration can be compared with the predicted titration curve for the full titration, using these "best values" for the macroscopic dissociation constants.

FORTRAN Program 14 is a simple and convenient way to compare a few data values with the numbers that the model predicts, for an assumed pair of equilibrium-constant values. This program reads a card on which are punched paired values of pH and titrant volume. The pH value is converted into a value of (H^+), and Equation 55 is used to calculate a predicted value of V_{NaOH}. The experimental and predicted values of volume are then printed, together with the corresponding pH value. Several sets of calculations, each with a slightly different value of one or both equilibrium constant(s), can be performed until you feel that the best agreement has been achieved.

• *Design a set of calculations to verify (or refute) the assertion that certain regions of the titrantion curve are the most sensitive regions with respect to variations in the numerical values of certain equilibrium constants.*

• *As an aid to finding the set of calculations that gives the best agreement, write a program that compares the calculated and predicted titrant volumes, perhaps by taking the difference, or the ratio, of these two numbers. If you want more significant figures in the output, what should you change in the program?*

• *Changing the value of* K_{HA^-} *has* <u>some</u> *effect on the predictions of the model in the vicinity of the first partial-equivalence point. Design a set of calculations (and perform the*

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// JOH                    S71007,S51


// FOR
*ONE WORD INTEGERS
* LIST SOURCE PROGRAM
*IOCS(CARD, 1132 PRINTER, TYPEWRITER, PLOTTER)
C       TITRATION CURVE

C       COMPARISON OF EXPERIMENTAL DATA WITH THE PREDICTIONS OF A
C       CHEMICAL MODEL

C       DIPROTIC ACID, ASSUMED VALUES OF KHA AND KHHA

C       DATA CARDS HAVE VMOH PUNCHED WITHIN THE FIRST 20 SPACES
C       DATA CARDS HAVE PH PUNCHED WITHIN THE SECOND 20 SPACES
C       INCLUDE DECIMAL POINT IN EACH VALUE OF VMOH AND PH
C       LAST DATA CARD MUST HAVE A NEGATIVE VALUE OF VMOH

        REAL KHA, KHHA, KW, NUM, MHA, MMOH
        KHHA = 1.1E-6
        KHA = 0.9E-7
        VHA = 25.00
        MHA = 0.0500
        MMOH = 0.1000
        KW = 1.008E-14
        CALL PREP (.2, .55, 1., 1.)
        WRITE (7,15) KHA, KHHA
     15 FORMAT ('KHHA = ',E8.2,'    KHA = ',E8.2)

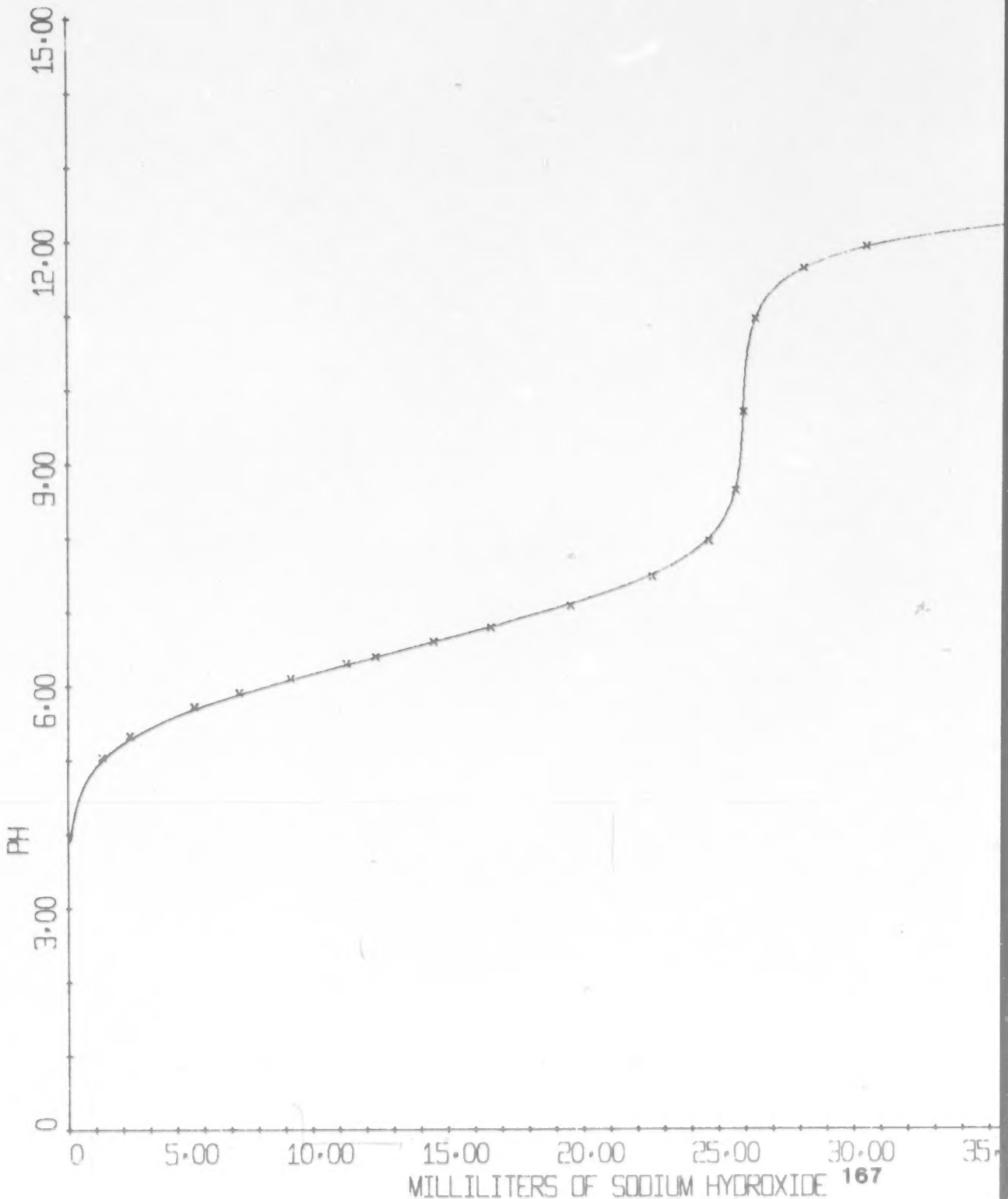
C       CALCULATION AND PLOTTING OF THE TITRATION CURVE
        H = 1.
      1 H = .5*H
        PH = -(ALOG(H))/2.303
        NUM = H**4 + KHHA*(H**3) + (KHHA*KHA - KHHA*MHA - KW)*(H**2)
       *-(2*KHHA*KHA*MHA + KW*KHHA)*H - KW*KHA*KHHA
        DEN = H**4 + (KHHA + MMOH)*(H**3) + (KHHA*KHA + KHHA*MMOH - KW)
       **(H**2) + (KHHA*KHA*MMOH - KW*KHHA)*H - KW*KHA*KHHA
        VMOH = -VHA*NUM/DEN
        IF (VMOH) 1,2,2
      2 CALL FPLOT (-2,VMOH,PH)
      5 H = H - .1*H
        PH = -(ALOG(H))/2.303
        NUM = H**4 + KHHA*(H**3) + (KHHA*KHA - KHHA*MHA - KW)*(H**2)
       *-(2*KHHA*KHA*MHA + KW*KHHA)*H - KW*KHA*KHHA
        DEN = H**4 + (KHHA + MMOH)*(H**3) + (KHHA*KHA + KHHA*MMOH - KW)
       **(H**2) + (KHHA*KHA*MMOH - KW*KHHA)*H - KW*KHA*KHHA
        VMOH = -VHA*NUM/DEN
        IF(50.-VMOH) 10,3,3
      3 CALL FPLOT (0,VMOH,PH)
        GO TO 5
```

```
C       PLOTTING DATA POINTS FROM THE TITRATI
   10 CONTINUE
   28 READ (2,25) V,P
   25 FORMAT (F20.2,F20.2)
      IF (V) 30,29,29
   29 CALL FPLOT (1,V,P)
      CALL FPLOT (-2,V,P)
      CALL POINT (1)
      GO TO 28

C       DRAWING AND LABELLING THE AXES
   30 CALL YAXIS (0., 0., 1., 10, 5)
      WRITE (7,17)
   17 FORMAT ('PH')
      CALL XAXIS (0.,0.,1.,50,10)
      WRITE (7,16)
   16 FORMAT ('MILLILITERS OF SODIUM HYDROXIDE')
      CALL FINPL
      CALL EXIT
      END


// XEQ
```

KHHA = 0.90E-07 KHA = 0.11E-05



calculations) to assess the effect of interations between the two equilibrium constants on the shape of the titration curve in regions that are critical for the evaluation of those equilibrium constants. The effect would be expected to be different, depending on the relative values (and on the absolute values) of the equilibrium constants.

A GRAPHICAL CONFRONTATION OF THE DATA AND THE MODEL

FORTRAN Program 15 allows you to compare data that you have punched on cards with predictions of the model in the form of data points placed on a calculated curve. Most people find the visual impact and effectiveness of this graphical presentation much greater than with a listing of numbers.

All the data used in the calculations whose output appears on page 167 were simulated, using the same algebraic equations but slightly different equilibrium-constant values. The data used in FORTRAN Program 14 were also obtained from a similar simulation, but with a third set of equilibrium-constant values. The numbers used are as follows:

	SIMULATED DATA	PROGRAM 14	PROGRAM 15
K_{H_2A}	1.0×10^{-6}	0.9×10^{-6}	1.1×10^{-6}
K_{HA^-}	1.0×10^{-7}	1.1×10^{-7}	0.9×10^{-7}

The difference between data and predictions is just barely detectable on the graph, whereas the numerical output shows the difference much more clearly. The overall effect can be grasped more readily by looking at the graph. Probably both methods can be used to advantage.

ASSESSING THE PRECISION OF EQUILIBRIUM-CONSTANT VALUES OBTAINED BY USING PROGRAMS 14 AND 15

An experimental scientist must always be concerned with the reliability and potential repeatability of his or her experiments and calculations. When a number is reported, he or she should indicate (by the number of significant figures in that number, or by a statement of the precision of that number) the probability that a repeat of the work by an independent investigator would yield the same number.

Thus it is important to see if two different equilibrium-constant values give equally-good fit of the data, within the limits of experimental uncertainties of the data. After you have found your "best value", you should repeat the calculation with a slightly altered value, checking to see if any significant variation occurs. If there is no discernible difference in the agreement obtained in using 1.0×10^{-6} and 1.1×10^{-6}, then it is misleading (and therefore not good science) to report a value as 1.00×10^{-6}, since the two zeros imply a knowledge of the digits that belong in those two decimal positions.

How can you estimate the "limits of experimental uncertainties of the data"? This is not always easy, but it is always important. For some guidance in assessing the limitations of burettes and pH meters, read over the information in Appendix II. Also keep asking yourself the question: "If I repeated the work, would I get the same answer a second (or third, or fourth) time?" If you don't know, then repeat some of the work and find out!

CAN A CLEARLY-INCORRECT MODEL GIVE A GOOD DESCRIPTION OF AN ACID-BASE TITRATION?

Throughout this case study, we have used a simple and straightforward criterion for testing a chemical or mathematical model: *"Do the predictions of the model agree, within the limits of experimental uncertainty, with experimental data?"* When there fails to be adequate agreement, this criterion signals the chemist that problems with either the model or the data (or both) exist. But what can be concluded when there is excellent agreement?

We shall investigate a clear case in which data are interpreted in terms of an incorrect model. In FORTRAN Program 16, we simulate data from the titration of a diprotic acid, marking these points with X marks on a piece of graph paper. Then, using the same axes, we plot as a smooth curve the predictions of a monoprotic-acid model. The results are shown on page 173. The data points lie precisely on the curve.

There is no way to tell, by analysis of titration data, whether this acid is a monoprotic acid with $K_{HA} = 0.5 \times 10^{-4}$, or a diprotic acid (present in half the molar concentration) with $K_{H_2A} = 1.0 \times 10^{-4}$ and $K_{HA^-} = 0.25 \times 10^{-4}$. The data are interpreted equally well with either model.

This is a special case, in which the diprotic acid equilibrium constants were chosen to stand in the ratio 1:4. But if we were to introduce some experimental uncertainty (some random scatter) into the data points, we might be able to apply an inappropriate model to a rather wide range of data. You can

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// JOB                  S71007,S51


// FOR
* LIST SOURCE PROGRAM
*IOCS(CARD, 1132 PRINTER, TYPEWRITER, PLOTTER)
*ONE WORD INTEGERS
C       DIPROTIC ACID DATA INTERPRETED VIA A MONOPROTIC MODEL
        REAL KHA, KHHA, KW, NUM, MHA, MMOH
        VHA = 25.00

        MHA = 0.0500
        MMOH = 0.1000
        KHHA = 1.E-4
        KHA = .25E-4
        KW = 1.008E-14
        CALL PREP (.2, .55, 1., 1.)
        WRITE (7,15)
   15 FORMAT ('DIPROTIC ACID DATA INTERPRETED VIA A MONOPROTIC ACID MODE
     *L')
        CALL YAXIS (0.,0.,1.,15,5)
        WRITE (7,17)
   17 FORMAT ('PH')
        CALL XAXIS (0., 0., 5., 7, 7)
        WRITE (7,16)
   16 FORMAT ('MILLILITERS OF SODIUM HYDROXIDE')

C       CALCULATION AND PLOTTING OF THE DIPROTIC TITRATION DATA POINTS
        H = 1.
    1   H = H - .1*H
        PH = -(ALOG(H))/2.303
        NUM = H**4 + KHHA*(H**3) + (KHHA*KHA - KHHA*MHA - KW)*(H**2)
       *-(2*KHHA*KHA*MHA + KW*KHHA)*H - KW*KHA*KHHA
        DEN = H**4 + (KHHA+MMOH)*(H**3) + (KHHA*KHA + KHHA*MMOH - KW)
       **(H**2) + (KHHA*KHA*MMOH - KW*KHHA)*H - KW*KHHA*KHA
        VMOH = -VHA*NUM/DEN
        IF (VMOH) 1,2,2
    2   CALL FPLOT (-2,VMOH,PH)
    5   H = H - .2*H
        PH = -(ALOG(H))/2.303
        NUM = H**4 + KHHA*(H**3) + (KHHA*KHA - KHHA*MHA - KW)*(H**2)
       *-(2*KHHA*KHA*MHA + KW*KHHA)*H - KW*KHHA*KHHA
        DEN = H**4 + (KHHA+MMOH)*(H**3) + (KHHA*KHA + KHHA*MMOH - KW)
       **(H**2) + (KHHA*KHA*MMOH - KW*KHHA)*H - KW*KHHA*KHA
        VMOH = -VHA*NUM/DEN
        IF (24.5-VMOH) 10,3,3
    3   CALL FPLOT (1,VMOH,PH)
        CALL FPLOT (-2,VMOH,PH)
        CALL POINT(1)
        GO TO 5

C       CALCULATION AND PLOTTING OF A MONOPROTIC TITRATION CURVE ON SAME AXES
   10   MHA = 2.*MHA
        KHA =0.5E-4
        H = 1.                                                    171
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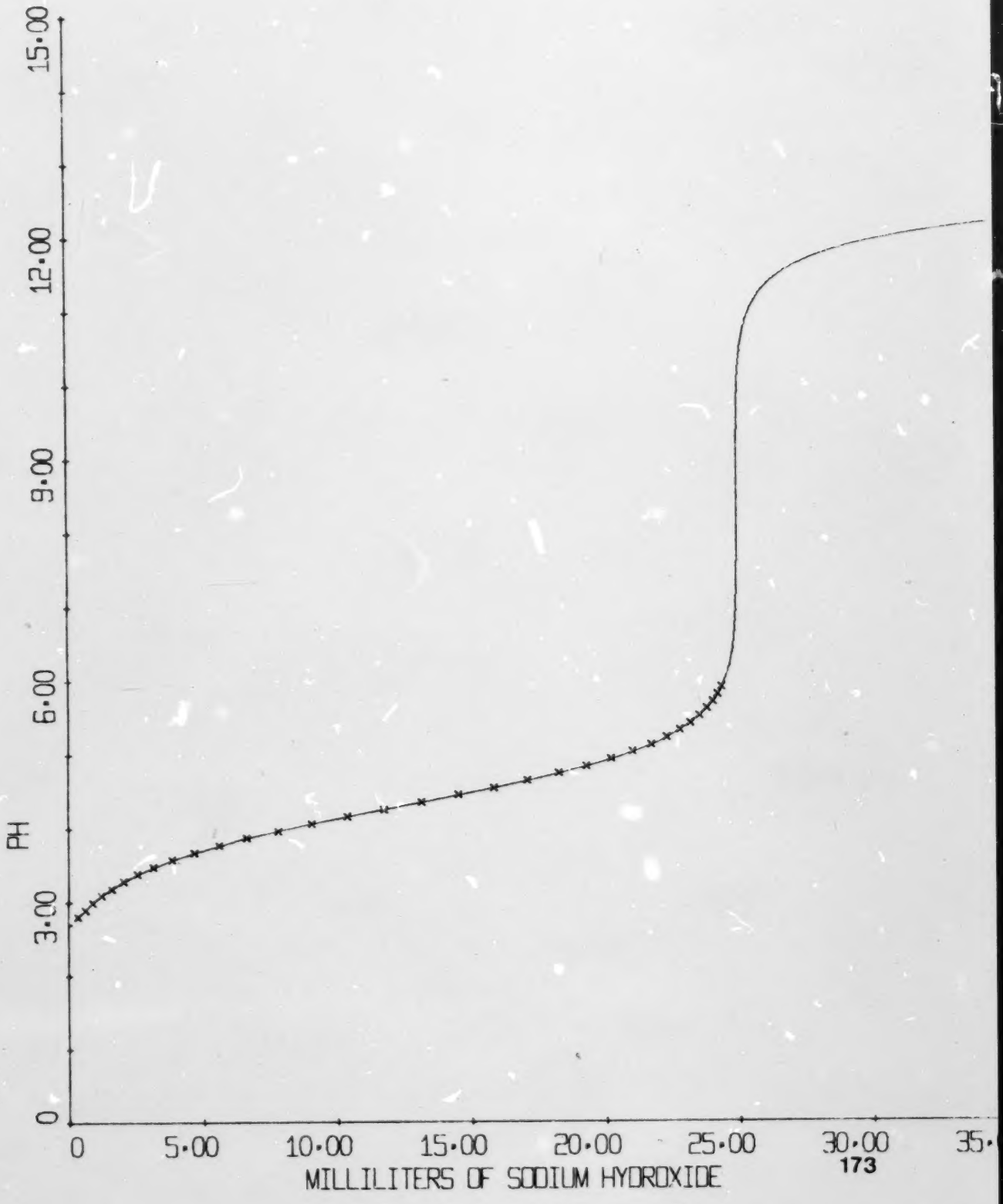
```
   51 H = .1*H
      PH = -(ALOG(H))/2.303
      NUM = H**3 + KHA*(H**2) - (KW + (KHA*MHA))*H - KW*KHA
      DEN =  H**3 + (KHA + MMOH)*(H**2) + (KHA*MMOH - KW)*H - KW*KHA
      VMOH = -VHA*NUM/DEN
      IF (VMOH) 51,52,52
   52 CALL FPLOT (1,VMOH,PH)
      CALL FPLOT (-2,VMOH,PH)
   55 H = H - .1*H
      PH = -(ALOG(H))/2.303
      DEN =  H**3 + (KHA + MMOH)*(H**2) + (KHA*MMOH - KW)*H - KW*KHA
      NUM = H**3 + KHA*(H**2) - (KW + (KHA*MHA))*H - KW*KHA
      VMOH = -VHA*NUM/DEN
      IF(35.-VMOH) 50,53,53
   53 CALL FPLOT (2,VMOH,PH)
      GO TO 55
   50 CALL FINPL
      CALL EXIT
      END

// XEQ
```

DIPROTIC ACID DATA INTERPRETED VIA A MONOPROTIC ACID MODEL



check on this possibility by incorporating some random scatter in the simulated data, and running FORTRAN Program 16 for various values of equilibrium constants. Check the IBM instruction manual for ways to generate a random variable to use in adding or subtracting random "errors" from the simulated data. How would you decide what value to use for the monoprotic-acid equilibrium constant?

This is a special case, as presented, but the problem is a general one throughout experimental science, and perhaps in all areas of knowledge. A careful investigator can often design a confrontation that shows a model for reality to be invalid, or inadequate. Such a model probably cannot be asserted to be "true." But the fact that a model is faithful (in all investigated respects) to reality does not provide proof or assurance of its truth.

WHAT IF K_{HA^-} WERE LARGER THAN K_{H_2A}?

The removal of a proton from a molecule results in an overall increase by one unit charge in the negative charge on that molecule This increase in negative charge (which is equivalent to a decrease in positive charge) results in a greater attraction (which is equivalent to a reduced repulsion) for remaining protons still bound to the molecule. These electrostatic considerations would be expected to make the successive microscopic equilibrium constants for removal of protons decrease in numerical value. The limiting situation would be the case of non-interacting, identical binding sites in which the sites are so far apart in space that electrostatic interactions are neglible; then the two successive microscopic dissociation constants are equal, the successive macroscopic dissociation constants differ by a factor of four, and $K_{H_2A} > K_{HA^-}$.

Removal of a proton does more than just increase negative charge. Changes in electronic configuration of the molecule are expected, and changes in the three-dimensional shape of the molecule are possible. And it may be reasonable to ask the question: *"What would happen if some changes altered the molecule so much that the successive microscopic equilibrium constants increase in numerical value?"* A search through tabulated values of macroscopic equilibrium constants has not revealed reports of any such instances. Maybe there are no such acids. Or maybe there is an alternative explanation.

CHEMISTS MAY HAVE BEEN MISLED BY THEIR OWN DATA

We shall present some results of a computer simulation that indicate

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PAGE    1  PARTIAL LISTING OF PROGRAM USED TO PREPARE GRAPH ON PAGE 177

// JOB T              S71007,S51

SMITH COLLEGE IBM 1130     MONITOR  VERSION 2  LEVEL 11  CORE SIZE  8K      06

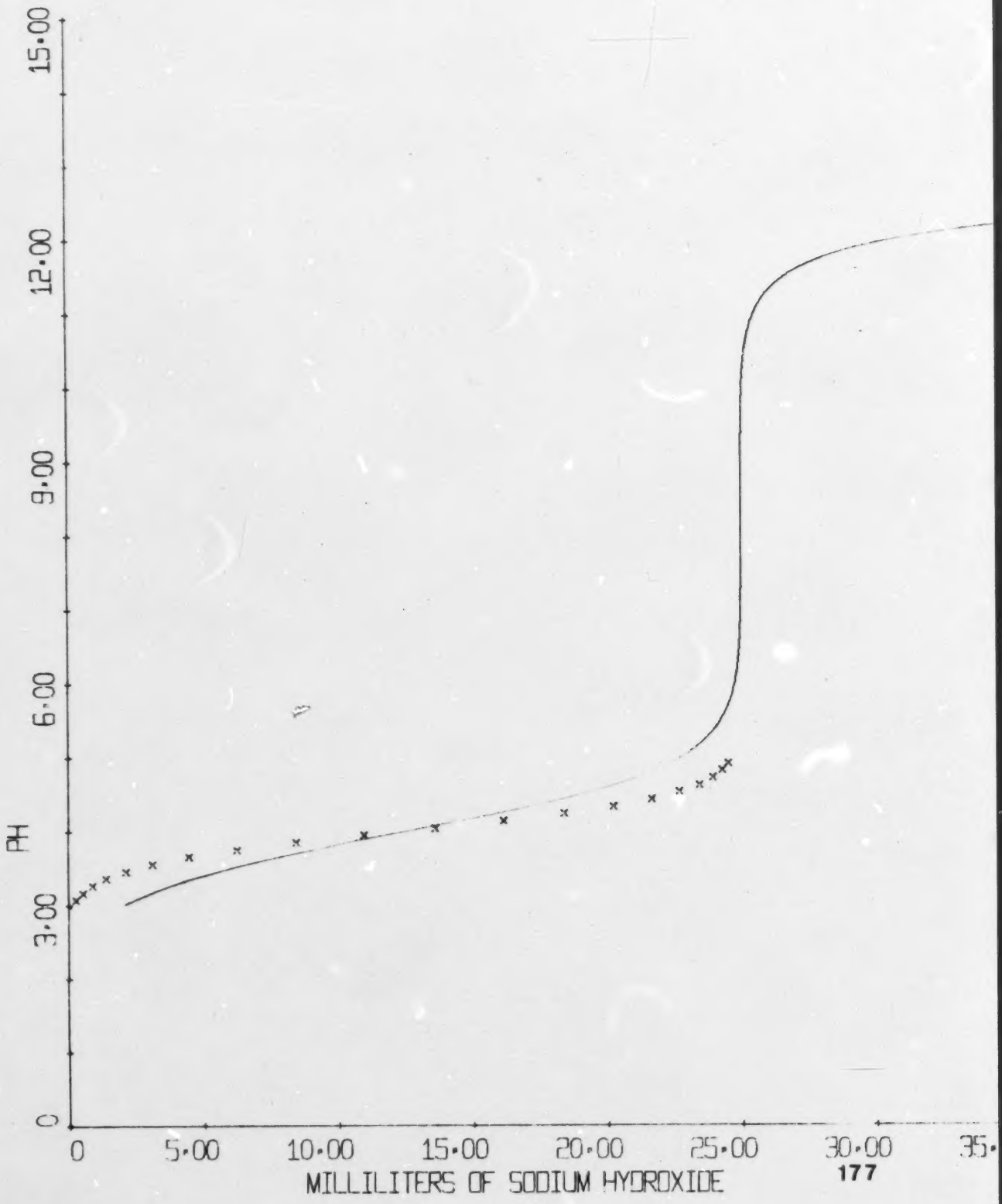
// FOR
* LIST SOURCE PROGRAM
*IOCS(CARD, 1132 PRINTER, TYPEWRITER, PLOTTER)
*ONE WORD INTEGERS
C       HOW WOULD WE KNOW IF THE SECOND K WERE LARGER THAN THE FIRST K
        REAL KHA, KHHA, KW, NUM, MHA, MMOH
        VHA = 25.00
        MHA = 0.0500
        MMOH = 0.1000
        KHHA = 1.E-5  <-
        KHA = 1.E-3   <-   Diprotic K's
        KW = 1.008E-14
        CALL PREP (.2, .55, 1., 1.)
        WRITE (7,15)
   15 FORMAT ('DIPROTIC ACID DATA INTERPRETED VIA A MONOPROTIC ACID MODE
      *L')
        CALL YAXIS (0.,0.,1.,15,5)
        WRITE (7,17)
   17 FORMAT ('PH')
        CALL XAXIS (0., 0., 5., 7, 7)
        WRITE (7,16)
   16 FORMAT ('MILLILITERS OF SODIUM HYDROXIDE')

C       CALCULATION AND PLOTTING OF THE DIPROTIC TITRATION DATA POINTS
        H = 1.
    1 H = H - .1*H
        PH = -(ALOG(H))/2.303
        NUM = H**4 + KHHA*(H**3) + (KHHA*KHA - KHHA*MHA - KW)*(H**2)
       *-(2*KHHA*KHA*MHA + KW*KHHA)*H - KW*KHA*KHHA
        DEN = H**4 + (KHHA+MMOH)*(H**3) + (KHHA*KHA + KHHA*MMOH - KW)
       **(H**2) + (KHHA*KHA*MMOH - KW*KHHA)*H - KW*KHHA*KHA
        VMOH = -VHA*NUM/DEN
        IF (VMOH) 1,2,2
    2 CALL FPLOT (-2,VMOH,PH)
    5 H = H - .2*H
        PH = -(ALOG(H))/2.303
        NUM = H**4 + KHHA*(H**3) + (KHHA*KHA - KHHA*MHA - KW)*(H**2)
       *-(2*KHHA*KHA*MHA + KW*KHHA)*H - KW*KHA*KHHA
        DEN = H**4 + (KHHA+MMOH)*(H**3) + (KHHA*KHA + KHHA*MMOH - KW)
       **(H**2) + (KHHA*KHA*MMOH - KW*KHHA)*H - KW*KHHA*KHA
        VMOH = -VHA*NUM/DEN
        IF (24.5-VMOH) 10,3,3
    3 CALL FPLOT (1,VMOH,PH)

        CALL FPLOT (-2,VMOH,PH)
        CALL POINT(1)
        GO TO 5

C       CALCULATION AND PLOTTING OF A MONOPROTIC TITRATION CURVE ON SAME AXES
   10 MHA = 2.*MHA
        KHA = 1.E-4  <- Monoprotic K
        H = 1.
```

DIPROTIC ACID DATA INTERPRETED VIA A MONOPROTIC ACID MODEL



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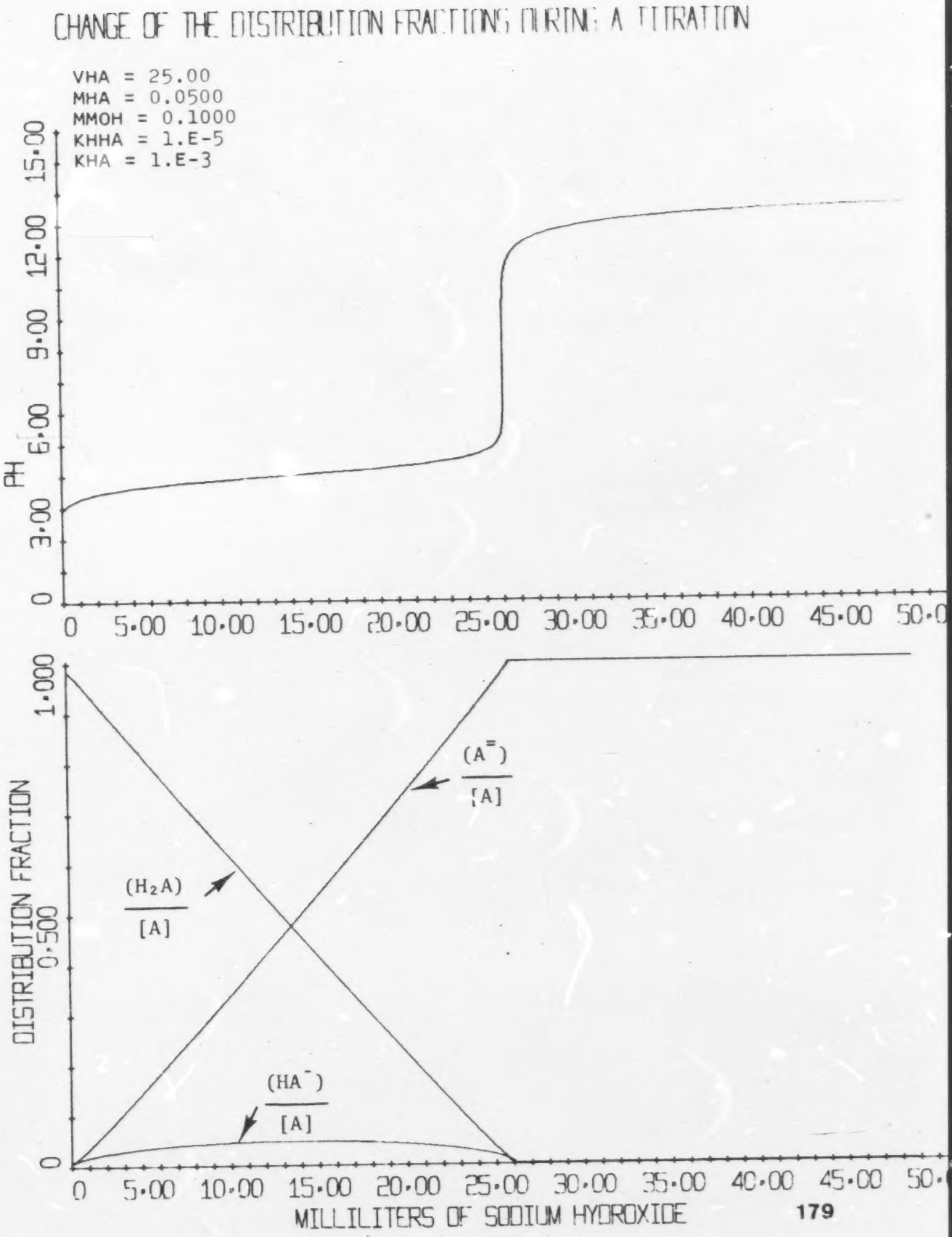
the possibility that a chemist could be led astray in interpreting experimental data from titration experiments if the acid were indeed diprotic with the second dissociation constant larger than the first. The computer-drawn graph on page 177 shows data calculated for an extreme case in which the equilibrium constants are in the atypical order, and differ by a factor of 100. The simulated data are indicated with X marks, and are compared with with a continuous curve, drawn on the same axes, calculated for a monoprotic acid, with twice the molar concentration, and with an equilibrium constant with pK the average of pK's of the diprotic equilibrium constants. (Some other value for the monoprotic K might have been more appropriate.)

If, as has been common in many research laboratories, only the half-equivalence point pH value(s) is used in evaluating the equilibrium constant(s), then this acid might be incorrectly interpreted as being a monoprotic acid with pK = 4, or as a diprotic acid with pK values in the normal order, equal to about 3.7 and 4.2. So maybe some such anomolous acids do exist, but have been missed by earlier investigators.

PREDICTIONS OF CHEMICAL PROPERTIES OF AN ACID WITH ATYPICAL ORDERING OF DISSOCIATION CONSTANTS

One of the most important features of simulation methods is the ability to make quantitative predictions about systems that have never been studied experimentally and which may in fact not exist. But *if there were an acid* with pK_{H_2A} = 5 and pK_{HA^-} = 3, then we can make some predictions on the basis of the information contained in the graphs on pages 177 and 179. The following features are worthy of note:


CHANGE OF THE DISTRIBUTION FRACTIONS DURING A TITRATION
VHA = 25.00
MHA = 0.0500
MMOH = 0.1000
KHHA = 1.E-5
KHA = 1.E-3
PH
0
3.00
6.00
9.00
12.00
15.00
0
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
50.0
DISTRIBUTION FRACTION
0
0.500
1.000
(A=)/[A]
(H2A)/[A]
(HA-)/[A]
0
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
50.
MILLILITERS OF SODIUM HYDROXIDE

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¶ A solution of this acid and its sodium salt would be an excellent buffer near pH 4. The slope of the titration curve in the interval 5 mℓ < V_{NaOH} < 20 mℓ is closer to zero than for any other of the titration curves in this case study.

¶ Since HA^- accounts for at most only five percent of the A-containing species in solution, the titration can be represented by the reaction

$$H_2A \rightleftarrows A^{=} + 2H^+$$

without serious error in the concentrations of H_2A and $A^{=}$. For discussion of the equilibrium properties of these solutions, considering only the reactants and products, there would seem to be no need to even mention the intermediate species. Can you write down the appropriate chemical model? What equilibrium constant would you use? Is there really any difference in the predicted shape of the titration curve?

¶ A Guess: Probably the shape of the titration curve would not be very much different if pK_{HA^-} were 2, or 1, or any smaller number. For larger values of this equilibrium constant, the distribution fraction $(HA^-)/[A]$ becomes even smaller. A numerical evaluation of this equilibrium constant from titration data becomes increasingly more difficult and less reliable as its value become larger. Can you check these guesses? How?

⇄ ⇄ ⇄ ⇄ ⇄

Chapter 3

Polyprotic Acid Equilibria

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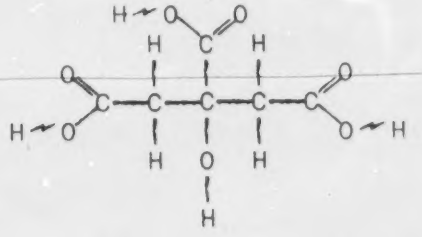
THE TITRATION OF CITRIC ACID IN AQUEOUS SOLUTION

Citric acid is the triprotic acid with the structure



We shall investigate the chemistry of citric acid from the point of view of the competition in water for protons. The competition for the limited number of available protons is among OH^- and each of the three carboxylate groups on citrate. This detailed examination involves a quantitative description of the distribution of chemical species throughout the course of a titration of a citric acid solution with a solution of sodium hydroxide. Our strategy in formulating a plausible, reasonable and verifiable description of the chemical system takes the form of the now-familiar sequence in which we

1. Propose a chemical model. This chemical model consists of a statement of the chemical species assumed to be present, and a collection of balanced chemical equations sufficient to permit interconversion of the species.
2. Formulate a mathematical model which embodies the relevant features of the chemical model. This mathematical model consists of a set of simultaneous algebraic equations.
3. Combine the algebraic equations to get an equation which relates experimentally-observable quantities, thus permitting a comparison of prediction with experiment.
4. Perform quantitative experiments to obtain numerical data for comparison with predictions.

If the predictions are consistent with experimental data, then

we shall consider that the model is an acceptable description of the chemical system. With citric acid, we shall find that the chemical model that we propose is not unique, and that many unreasonable models will give rise to the same prediction of the experimentally-observed titration curve. Some chemical judgment is required, and some data from non-titration experiments, as well as comparative titration data from certain related compounds, becomes very helpful in making the test of reasonableness.

The proton dissociation equilibria for citric acid can be schematically diagrammed as in Figure 1. It is possible to define even more microscopic equilibria, but the collection of explicitly-written reactions and associated equilibrium constants given in Figure 2 includes more than enough K's to describe completely the distribution of species in a solution of citric acid at any pH value. It includes many more K's than are required to calculate a titration curve, and in fact we shall soon find that only three equilibrium constants are required in order to *describe the macroscopic titration phenomena*. The many additional equilibrium constants are introduced in order to *interpret* the phenomena.

PREDICTION OF THE SHAPE OF THE TITRATION CURVE

For the prediction of the titration curve, we need a chemical model written in terms of only the macroscopic equilibria. The following chemical equations suffice. Written with each chemical equation is the associated equilibrium-constant equation that forms a part of the mathematical model for the titration.

$$H_3C \rightleftarrows H_2C^- + H^+ \qquad K_A = \frac{(H_2C^-)(H^+)}{(H_3C)} \tag{74}$$

$$H_2C^- \rightleftarrows HC^{-2} + H^+ \qquad K_B = \frac{(HC^{-2})(H^+)}{(H_2C^-)} \tag{75}$$

$$HC^{-2} \rightleftarrows C^{-3} + H^+ \qquad K_C = \frac{(C^{-3})(H^+)}{(HC^{-2})} \tag{76}$$

$$H_2O \rightleftarrows H^+ + OH^- \qquad K_w = (H^+)(OH^-) \tag{77}$$

The two conservation equations are

$$[C] = (H_3C) + (H_2C^-) + (HC^{-2}) + (C^{-3}) \tag{78}$$

$$[M] = (M^+) \tag{79}$$

The electroneutrality equation is

$$(H^+) + (M^+) = (OH^-) + (H_2C^-) + 2(HC^{-2}) + 3(C^{-3}) \tag{80}$$

An equation for the titration curve can be obtained by using Equations 74 — 79 to eliminate the individual species concentrations from Equation 80, producing an equation in which only the concentrations [C], [M], and (H^+) appear; and then introducing volume variables. A great deal of algebra is simplified if we make use of the results of the next section on distribution fractions. So we interrupt this derivation for a digression.

DISTRIBUTION FRACTIONS IN TERMS OF THE MACROSCOPIC EQUILIBRIA Proceeding exactly as we have before in the cases of monoprotic and diprotic acids, we find the distribution fractions by starting with Equation 78, and then using the equilibrium-constant equations to eliminate all but one of the species concentrations. Thus we can write Equation 78 as

Figure 1

A SCHEMATIC PROTON DISSOCIATION SCHEME FOR CITRIC ACID

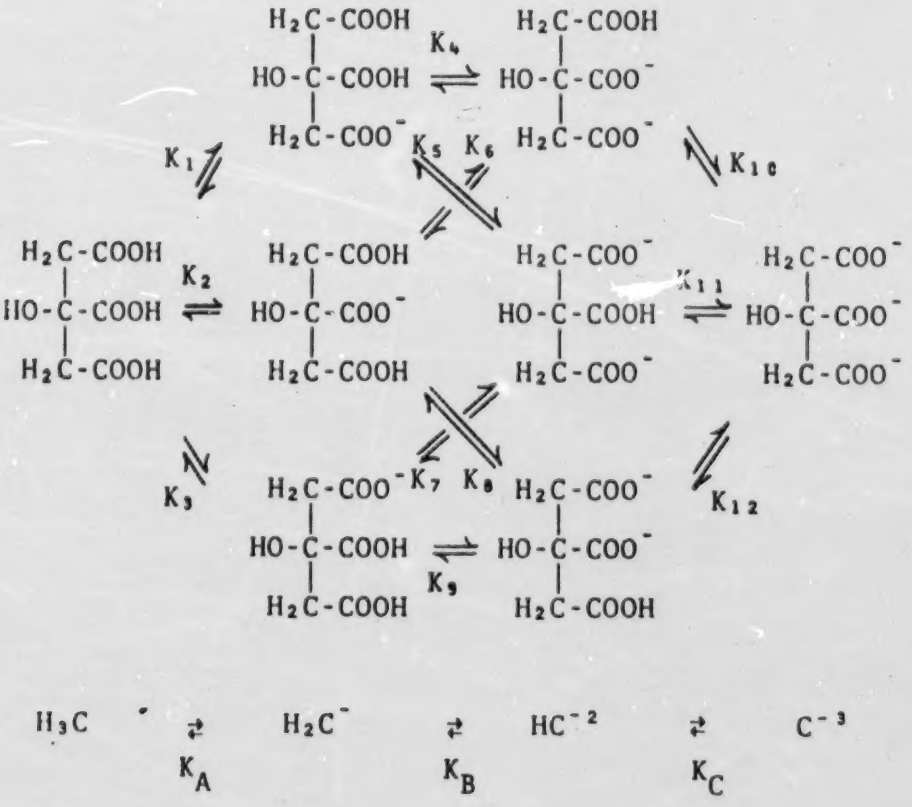


Figure 2

MICROSCOPIC EQUILIBRIA IN THE CHEMICAL MODEL FOR CITRIC ACID

$$\begin{matrix} H & H \\ H & \rightleftarrows & H & + & H^+ \\ H & & - \end{matrix} \qquad K_1 = \frac{\begin{pmatrix} H \\ H \\ - \end{pmatrix}(H^+)}{\begin{pmatrix} H \\ H \\ H \end{pmatrix}}$$

$$\begin{matrix} H & H \\ H & \rightleftarrows & - & + & H^+ \\ H & & H \end{matrix} \qquad K_2 = \frac{\begin{pmatrix} H \\ - \\ H \end{pmatrix}(H^+)}{\begin{pmatrix} H \\ H \\ H \end{pmatrix}}$$

$$\begin{matrix} H & - \\ H & \rightleftarrows & H & + & H^+ \\ H & & H \end{matrix} \qquad K_3 = \frac{\begin{pmatrix} - \\ H \\ H \end{pmatrix}(H^+)}{\begin{pmatrix} H \\ H \\ H \end{pmatrix}}$$

$$\begin{matrix} H & H \\ H & \rightleftarrows & - & + & H^+ \\ - & & - \end{matrix} \qquad K_4 = \frac{\begin{pmatrix} H \\ - \\ - \end{pmatrix}(H^+)}{\begin{pmatrix} H \\ H \\ - \end{pmatrix}}$$

$$\begin{matrix} H & - \\ H & \rightleftarrows & H & + & H^+ \\ - & & - \end{matrix} \qquad K_5 = \frac{\begin{pmatrix} - \\ H \\ - \end{pmatrix}(H^+)}{\begin{pmatrix} H \\ H \\ - \end{pmatrix}}$$

$$\begin{matrix} H & H \\ - & \rightleftarrows & - & + & H^+ \\ H & & - \end{matrix} \qquad K_6 = \frac{\begin{pmatrix} H \\ - \\ - \end{pmatrix}(H^+)}{\begin{pmatrix} H \\ - \\ H \end{pmatrix}}$$

$$\begin{matrix} - & - \\ H & \rightleftarrows & H & + & H^+ \\ H & & - \end{matrix} \qquad K_7 = \frac{\begin{pmatrix} - \\ H \\ - \end{pmatrix}(H^+)}{\begin{pmatrix} - \\ H \\ H \end{pmatrix}}$$

$$\begin{matrix} H & - \\ - & \rightleftarrows & - & + & H^+ \\ H & & H \end{matrix} \qquad K_8 = \frac{\begin{pmatrix} - \\ - \\ H \end{pmatrix}(H^+)}{\begin{pmatrix} H \\ - \\ H \end{pmatrix}}$$

$$\begin{matrix} - & - \\ H & \rightleftarrows & - & + & H^+ \\ H & & H \end{matrix} \qquad K_9 = \frac{\begin{pmatrix} - \\ - \\ H \end{pmatrix}(H^+)}{\begin{pmatrix} - \\ H \\ H \end{pmatrix}}$$

$$\begin{matrix} H & - \\ - & \rightleftarrows & - & + & H^+ \\ - & & - \end{matrix} \qquad K_{10} = \frac{\begin{pmatrix} - \\ - \\ - \end{pmatrix}(H^+)}{\begin{pmatrix} H \\ - \\ - \end{pmatrix}}$$

$$\begin{matrix} - & - \\ H & \rightleftarrows & - & + & H^+ \\ - & & - \end{matrix} \qquad K_{11} = \frac{\begin{pmatrix} - \\ - \\ - \end{pmatrix}(H^+)}{\begin{pmatrix} - \\ H \\ - \end{pmatrix}}$$

$$\begin{matrix} - & - \\ - & \rightleftarrows & - & + & H^+ \\ H & & - \end{matrix} \qquad K_{12} = \frac{\begin{pmatrix} - \\ - \\ - \end{pmatrix}(H^+)}{\begin{pmatrix} - \\ - \\ H \end{pmatrix}}$$

$$[C] = (H_3C) + (H_3C)K_A/(H^+) + (H_3C)K_AK_B/(H^+)^2 + (H_3C)K_AK_BK_C/(H^+)$$

$$= (H_3C)\{1 + K_A/(H^+) + K_AK_B/(H^+)^2 + K_AK_BK_C/(H^+)^3\}$$

$$(H^+)^3[C] = (H_3C)\{(H^+)^3 + K_A(H^+)^2 + K_AK_B(H^+) + K_AK_BK_C\} \quad (81)$$

In like manner, we get Equation 78 in terms of the concentration (H_2C^-) to give

$$K_A(H^+)^2[C] = (H_2C^-)\{(H^+)^3 + K_A(H^+)^2 + K_AK_B(H^+) + K_AK_BK_C\} \quad (82)$$

It is significant that the quantity in { } is the same in both Equations 81 and 82. In fact, this same factor appears again when we write Equation 78 in terms of (HC^{-2}) or in terms of (C^{-3}). Let us therefore define this factor as F_{den}:

$$F_{den} = (H^+)^3 + K_A(H^+)^2 + K_AK_B(H^+) + K_AK_BK_C \quad (83)$$

and then write each of the distribution fractions as a fraction with the denominator F_{den}. The four resulting equations are

$$\frac{(H_3C)}{[C]} = \frac{(H^+)^3}{F_{den}} \qquad \frac{(H_2C^-)}{[C]} = \frac{(H^+)^2K_A}{F_{den}} \quad (84)$$

$$\frac{(HC^{-2})}{[C]} = \frac{(H^+)K_AK_B}{F_{den}} \qquad \frac{(C^{-3})}{[C]} = \frac{K_AK_BK_C}{F_{den}}$$

RETURN TO THE TITRATION CURVE

We now use Equations 77, 78, 79, and 84 to transform Equation 80 into

$$(H^+) + [M] - K_w/(H^+) = \{(H^+)^2K_A + 2(H^+)K_AK_B + 3K_AK_BK_C\}/F_{den}$$

Multiplication of both sides of the equation by F_{den}, followed by rearrangement of terms, yields

$$(H^+)^5 + (H^+)^4\{[M] + K_A\} + (H^+)^3\{K_A[M] - K_A[C] + K_AK_B - K_w\}$$

$$+ (H^+)^2\{K_AK_B[M] - 2K_AK_B[C] + K_AK_BK_C - K_AK_w\} \quad (85)$$

$$+ (H^+)\{K_AK_BK_C[M] - 3K_AK_BK_C[C] - K_AK_BK_w\} - K_AK_BK_CK_w = 0$$

Recognizing that the two concentrations [M] and [C] are not independent during a titration, we decide to change variables so as to have a single independent variable. The natural choice for this independent variable is the volume of titrant which has been dispensed from the burette. The change of variables is accomplished by utilizing the relationships

$$[M] = \frac{V_{MOH}M_{MOH}}{V_{MOH} + V_{HA}} \qquad [C] = \frac{V_{HA}M_{HA}}{V_{MOH} + V_{HA}} \tag{86}$$

Introduction of Equations 86 into Equation 85 results in

$$V_{MOH} = -V_{HA}\left[\frac{\begin{array}{l}(H^+)^5 + (H^+)^4K_A + (H^+)^3\{K_AK_B - K_w - K_AM_{HA}\} \\ + (H^+)^2\{K_AK_BK_C - K_AK_w - 2K_AK_BM_{HA}\} \\ - (H^+)\{K_AK_BK_w + 3K_AK_BK_CM_{HA}\} - K_AK_BK_CK_w\end{array}}{\begin{array}{l}(H^+)^5 + (H^+)^4\{M_{MOH} + K_A\} + (H^+)^3\{K_AM_{MOH} + K_AK_B - K_w\} \\ + (H^+)^2\{K_AK_BM_{MOH} + K_AK_BK_C - K_AK_w\} \\ + (H^+)\{K_AK_BK_CM_{MOH} - K_AK_BK_w\} - K_AK_BK_CK_w\end{array}}\right] \tag{87}$$

Equation 87 is in the usual form which we have been using for computer-assisted calculation of titration curves.

Without any consideration of the microscopic equilibria, we have been able to make a quantitative prediction of the data which would be obtained in an experimental titration. The description of the observable phenomena has been made in terms of Equation 87 which is a *phenomenological equation* written in terms of four *phenomenological equilibrium constants*. We consider as synonyms the terms

phenomenological equilibrium constant
macroscopic equilibrium constant
experimentally-observable equilibrium constant

Each macroscopic equilibrium constant may describe a process that is a superposition of several of the microscopic chemical reactions of the original model. The microscopic reactions, and the individual chemical species used in formulating the model for the reaction of protons with the variously-protonated citrate ions, are not directly, explicitly or unambiguously observed by casual inspection of the titration curve of citric acid. To analyze a titration curve, we first decide to treat citric acid as a triprotic acid, and obtain Equation 87. We then extract numerical values of three macroscopic equilibrium constants from an experimental titration curve. Then, supplying additional information not contained in the titration data, we try to interpret these three macroscopic equilibrium constants in terms of the many reactions in Figure 2.

RELATIONSHIPS BETWEEN THE MACROSCOPIC AND THE MICROSCOPIC EQUILIBRIUM CONSTANTS FOR CITRIC ACID

Equations 74, 75, and 76 are not written with the same symbols as the dozen equations in Figure 2. We need to make a translation between the macroscopic language and the microscopic language, and we now do so via the definitions:

$$(H_3C) \equiv \text{sum of the concentrations of all triply-protonated citrate species} = \begin{pmatrix} H \\ H \\ H \end{pmatrix} \tag{88}$$

$$(H_2C^-) \equiv \text{sum of the concentrations of all doubly-protonated citrate species} = \begin{pmatrix} H \\ H \\ - \end{pmatrix} + \begin{pmatrix} H \\ - \\ H \end{pmatrix} + \begin{pmatrix} - \\ H \\ H \end{pmatrix} \tag{89}$$

$$(HC^{-2}) \equiv \text{sum of the concentrations of all singly-protonated citrate species} = \begin{pmatrix} H \\ - \\ - \end{pmatrix} + \begin{pmatrix} - \\ H \\ - \end{pmatrix} + \begin{pmatrix} - \\ - \\ H \end{pmatrix} \tag{90}$$

$$(C^{-3}) \equiv \text{sum of the concentrations of all unprotonated citrate species} = \begin{pmatrix} - \\ - \\ - \end{pmatrix} \tag{91}$$

Direct substitution of definitions 88 — 91 into Equations 74, 75 and 76 results in

$$K_A = \frac{\left(\begin{pmatrix}H\\H\\-\end{pmatrix} + \begin{pmatrix}H\\-\\H\end{pmatrix} + \begin{pmatrix}-\\H\\H\end{pmatrix}\right)(H^+)}{\begin{pmatrix}H\\H\\H\end{pmatrix}} \tag{92}$$

$$K_AK_B = \frac{(HC^{-2})(H^+)^2}{(H_3C)} = \frac{\left(\begin{pmatrix}H\\-\\-\end{pmatrix} + \begin{pmatrix}-\\H\\-\end{pmatrix} + \begin{pmatrix}-\\-\\H\end{pmatrix}\right)(H^+)^2}{\begin{pmatrix}H\\H\\H\end{pmatrix}} \tag{93}$$

$$K_AK_BK_C = \frac{(C^{-3})(H^+)^3}{(H_3C)} = \frac{\begin{pmatrix}-\\-\\-\end{pmatrix}(H^+)^3}{\begin{pmatrix}H\\H\\H\end{pmatrix}} \tag{94}$$

Inspection of Figure 2 reveals various ways in which the microscopic equilibrium constant equations can be combined with Equations 92, 93, and 94. For instance, we find that

$$K_A = K_1 + K_2 + K_3$$

$$\begin{aligned} K_AK_B &= K_1K_4 + K_2K_6 + K_3K_9 \\ &= K_1K_4 + K_1K_5 + K_2K_8 \\ &= K_2K_6 + K_2K_8 + K_3K_7 \\ &= \text{other combinations of microscopic equilibrium constants} \end{aligned}$$

$$\begin{aligned} K_AK_BK_C &= K_1K_4K_{10} \\ &= K_2K_6K_{10} \\ &= \text{many other combinations of microscopic constants} \end{aligned}$$

There are more independent microscopic equilibrium constants than there are macroscopic equilibrium constants, and therefore experimental titration data alone contain insufficient information for numerical evaluation of the microscopic constants. There are many sets of values of the microscopic constants that are fully consistent with the experimental values for the three macroscopic equilibrium constants.

DISTRIBUTION FRACTIONS IN TERMS OF THE MICROSCOPIC EQUILIBRIA

The fraction of all citrate-containing species present as the microscopic species

$$\begin{pmatrix} H \\ H \\ H \end{pmatrix}$$

is given by the first of Equations 84, since by definition 88

$$\begin{pmatrix} H \\ H \\ H \end{pmatrix} = (H_3C)$$

We thus have

$$F_{H_3C} \equiv \frac{\begin{pmatrix} H \\ H \\ H \end{pmatrix}}{[C]} = \frac{(H^+)^3}{F_{den}} \qquad (95)$$

Combination of Equation 95 with the defining equations for K_1, K_2, and K_3 from Figure 2 gives

$$F_{H_2C1} \equiv \frac{\begin{pmatrix} H \\ H \\ - \end{pmatrix}}{[C]} = F_{H_3C}K_1/(H^+) \qquad (96)$$

$$F_{H_2C2} \equiv \frac{\begin{pmatrix} H \\ - \\ H \end{pmatrix}}{[C]} = F_{H_3C}K_2/(H^+) \qquad (97)$$

$$F_{H_3C3} \quad \frac{\begin{pmatrix} - \\ H \\ H \end{pmatrix}}{[C]} = F_{H_3C} K_3/(H^+) \qquad (98)$$

• *Find equations for computing the distribution fractions for the remaining microscopic species. Compare your results with the equations used in FORTRAN Program 17 for calculating these distribution fractions.*

A FORTRAN PROGRAM FOR CALCULATING THE MICROSCOPIC DISTRIBUTION FRACTIONS DURING THE TITRATION OF CITRIC ACID WITH SODIUM HYDROXIDE

FORTRAN Program 17 gives a prediction of each of the microscopic distribution fractions during a simulated titration of citric acid with a solution of sodium hydroxide. Numerical values of seven of the microscopic equilibrium constants are introduced. The molecular symmetry of citric acid is invoked, allowing us to equate each of the remaining five micro constants with one of the initial seven. Equations such as those developed on page 190 are used to calculate values for the three macroscopic equilibrium constants, and these constants are used with Equation 87 for the calculation of the titration curve. At each pH value on the titration curve, Equations such as 96, 97, or 98 are used to calculate each of the microscopic equilibrium constants.

Format statement 11 has two programming features that make the output a little neater and more legible. In our previous format statements for the printer beginning with information within ' ' marks, the first character with the ' ' has been a blank. This time the numeral 1 appears, and this 1 is an instruction for the printer to advance to a new page of paper. Appearing

17

```
// JOB                    S71007,S51


// FOR
* LIST SOURCE PROGRAM
*IOCS(CARD, 1132 PRINTER)
      REAL NUM, KA, KB, KC, KW, MMOH, MHA, K1, K2, K3, K4, K5, K6, K7,
     *K8, K9, K10, K11, K12
C     CALCULATION OF FRACTIONS OF TOTAL CITRATE-CONTAINING SPECIES
C     PRESENT AS EACH OF THE MICROSCOPIC SPECIES DURING THE TITRATION
C     OF CITRIC ACID
      K1 = 10**(-3.85)
      K2 = 10**(-3.35)
      K4 = 10**(-4.60)
      K5 = 10**(-4.40)
      K6 = 10**(-5.10)
      K10 = 10**(-5.85)
      K11 = 10**(-6.05)
      K3 = K1
      K7 = K5
      K8 = K6
      K9 = K4
      K12 = K10
      KW = 1.008E-14
      KA = 2.*K1 + K2
      KB = (K1*K5 + 2.*K2*K6)/KA
      KC = (K1*K4*K10)/(KA*KB)
      PKA = -(ALOG(KA))/2.303
      PKB = -(ALOG(KB))/2.303
      PKC = -(ALOG(KC))/2.303
      WRITE (3,11) PKA, PKB, PKC
   11 FORMAT ('1PKA =', F6.2, '     PKB =', F6.2, '     PKC =', F6.2//)
      VHA = 10.00
      MHA = .100
      MMOH = .100
      H = 1.
    1 H = H - .1*H
      NUM = H**5 + (H**4)*KA + (H**3)*(KA*KB - KW - KA*MHA) +
     *(H**2)*(KA*KB*KC - KW*KA - 2.*KA*KB*MHA) - H*(KA*KB*KW +
     *3.*KA*KB*KC*MHA) - KA*KB*KC*KW
      DEN = (H**5) + (H**4)*(MMOH + KA) + (H**3)*(KA*MMOH - KW + KA*KB)
     *+ (H**2)*(KA*KB*MMOH - KW*KA + KA*KB*KC) + H*(KA*KB*KC*MMOH -
     *KA*KB*KW) - KA*KB*KC*KW
      VMOH = -VHA*NUM/DEN
      IF (VMOH) 1,2,2
    2 FDEN = (H**3) + KA*H*H + KA*KB*H + KA*KB*KC
      FH3C = (H**3)/FDEN
      FH2C = KA*(H**2)/FDEN
      FH2C = KA*(H**2)/FDEN
      FHC = KA*KB*H/FDEN
      FC = KA*KB*KC/FDEN
      FH2C1 = K1*FH3C/H
      FH2C2 = K2*FH3C/H
      FH2C3 = K3*FH3C/H
      FHC1 = FC*H/K10
```

```
      FHC2 = FC*H/K11
      FHC3 = FC*H/K12
      PH = -(ALOG(H))/2.303
      WRITE(3,12) FH3C, FH2C1, FH2C2, FH2C3, FHC1, FHC2, FHC3, FC, VMOH,
     *PH
   12 FORMAT (FC.5,3X,3F9.5,3X,3F9.5,3X,F9.5,3X,F8.2,F5.2)
      H = H -.5*H
      NUM = H**5 + (H**4)*KA + (H**3)*(KA*KB - KW - KA*MHA) +
     *(H**2)*(KA*KB*KC - KW*KA - 2.*KA*KB*MHA) - H*(KA*KB*KW +
     *3.*KA*KB*KC*MHA) - KA*KB*KC*KW
      DEN = (H**5) + (H**4)*(MMOH + KA) + (H**3)*(KA*MMOH - KW + KA*KB)
     ** (H**2)*(KA*KB*MMOH - KW*KA + KA*KB*KC) + H*(KA*KB*KC*MMOH -
     *KA*KB*KW) - KA*KB*KC*KW
      VMOH = -VHA*NUM/DEN
      IF (VMOH) 30,2,2
   30 CALL EXIT
      END

// XEQ
```

PKA = 3.13 PKB = 4.75 PKC = 6.40

0.91487	0.01645	0.05202	0.01645	0.00005	0.00008	0.00005	0.00000	0.00	2.10
0.84282	0.03031	0.09585	0.03031	0.00019	0.00030	0.00019	0.00000	1.14	2.40
0.72747	0.05232	0.16547	0.05232	0.00066	0.00106	0.00066	0.00000	2.50	2.70
0.56952	0.08193	0.25909	0.08193	0.00209	0.00332	0.00209	0.00000	4.24	3.00
0.39399	0.11335	0.35847	0.11335	0.00579	0.00919	0.00579	0.00001	6.18	3.30
0.23917	0.13759	0.43512	0.13759	0.01408	0.02231	0.01408	0.00008	8.07	3.60
0.12833	0.14777	0.46729	0.14777	0.03024	0.04793	0.03024	0.00034	9.78	3.91
0.06141	0.14137	0.44705	0.14137	0.05786	0.09171	0.05786	0.00133	11.47	4.21
0.02600	0.11973	0.37863	0.11973	0.09801	0.15534	0.09801	0.00451	13.33	4.51
0.00981	0.08856	0.28007	0.08856	0.14500	0.22981	0.14500	0.01335	15.36	4.81
0.00337	0.05695	0.18010	0.05695	0.18649	0.29557	0.18649	0.03434	17.33	5.11
0.00087	0.03217	0.10175	0.03217	0.21072	0.33397	0.21072	0.07760	19.09	5.41
0.00021	0.01618	0.05118	0.01618	0.21201	0.33602	0.21201	0.15016	20.72	5.71
0.00004	0.00726	0.02297	0.00726	0.19028	0.30157	0.19028	0.28030	22.42	6.01
0.00000	0.00287	0.00910	0.00287	0.15083	0.23905	0.15083	0.44439	24.29	6.31
0.00000	0.00100	0.00316	0.00100	0.10496	0.16636	0.10496	0.61852	26.13	6.61
0.00000	0.00030	0.00098	0.00030	0.06495	0.10295	0.06495	0.76553	27.63	6.92
0.00000	0.00008	0.00027	0.00008	0.03680	0.05833	0.03680	0.86758	28.67	7.22
0.00000	0.00002	0.00007	0.00002	0.01971	0.03124	0.01971	0.92921	29.29	7.52
0.00000	0.00000	0.00001	0.00000	0.01021	0.01619	0.01021	0.96333	29.63	7.82
0.00000	0.00000	0.00000	0.00000	0.00520	0.00824	0.00520	0.98133	29.81	8.12
0.00000	0.00000	0.00000	0.00000	0.00262	0.00416	0.00262	0.99058	29.90	8.42
0.00000	0.00000	0.00000	0.00000	0.00131	0.00209	0.00131	0.99526	29.95	8.72
0.00000	0.00000	0.00000	0.00000	0.00066	0.00104	0.00066	0.99762	29.98	9.02
0.00000	0.00000	0.00000	0.00000	0.00033	0.00052	0.00033	0.99881	29.99	9.32
0.00000	0.00000	0.00000	0.00000	0.00016	0.00026	0.00016	0.99940	30.01	9.62
0.00000	0.00000	0.00000	0.00000	0.00008	0.00013	0.00008	0.99970	30.03	9.92
0.00000	0.00000	0.00000	0.00000	0.00004	0.00006	0.00004	0.99985	30.06	10.23
0.00000	0.00000	0.00000	0.00000	0.00002	0.00003	0.00002	0.99992	30.13	10.53
0.00000	0.00000	0.00000	0.00000	0.00001	0.00001	0.00001	0.99996	30.27	10.83
0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.99998	30.55	11.13
0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.99999	31.13	11.43
0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.99999	32.33	11.73
0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.99999	34.95	12.03
0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.99999	41.31	12.33
0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.99999	61.54	12.63
0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.99999	328.50	12.93

at the end of the statement is //, telling the printer to advance two lines.

The computing capacity of the IBM 1130 system is exceeded during the calculation of NUM and DEN for very small values of (H^+). As an example, at pH 11, $(H^+) = 10^{-11}$ and $(H^+)^5 = 10^{-55}$. This computer cannot handle such a small number, but happily the failure is fail-safe failure for us, since the computer treats the very small number as zero. This would pose serious problems for some calculations, but not for us at this time. Each of these very small numbers enters as an insignificantly-small term in an indicated sum, the sum containing other terms that are properly calculated, and no significant error results in the sum.

The output would be easier to read if a caption had been printed over the columns of numbers. Such a caption could have been printed by using a WRITE statement just after format statement 11.

ABOUT COMMONALITY OF CHEMICAL SPECIES

The mathematical model for this system is formulated by describing the equilibrium system as involving many independent chemical reactions, each reaction characterized by a microscopic equilibrium constant. Coupling of these independent chemical reactions is accomplished through the requirements of

¶Conservation of mass

¶Electroneutrality

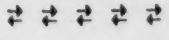
¶Commonality of chemical species

The phrase *commonality of species* means that a chemical symbol has the same meaning in each of its appearances in chemical equa-

tions, and that the corresponding concentration has the same numerical value in each of the algebraic equations in which it appears. This means, among other things, that the pool of that species is available at the same concentration to all reactants. When that species is produced by a reaction, it becomes distributed throughout the solution. The requirement of commonality of species might fail to be satisfied in an intra-molecular reaction during which a group was transferred between two regions of a molecule without ever being released into the main bulk of the solution as a free and independent species.

A valuable research paper that should be read in conjunction with this section is R. B. Martin, "A Complete Ionization Scheme for Citric Acid," The Journal of Physical Chemistry, vol. 65, pp. 2053 - 2055 (1961). Details are given of the experiments and the assumptions required for estimating values of the microscopic equilibrium constants for citric acid.

Equilibria involved in the titration of the amino acid tyrosine involves twelve microscopic equilibrium constants, and all twelve have been evaluated from experimental data and a set of plausible assumptions. Details are given in R. B. Martin, J. T. Edsall, D. B. Wetlaufer, and B. R. Hollingworth, Journal of Biological Chemistry, vol. 233, pp. 1429ff (1958)



DESIGNING YOUR OWN RESEARCH PROJECT INVOLVING CARBOXYLIC ACIDS AND MULTIPLE EQUILIBRIA

One way to plan a research project is to begin by reading some relevant research papers relating to the system that you intend to study. Some excellent sources of references to such papers are given on page 61. Many common diprotic and polyprotic acids have been studied only in passing, as parts of research projects that other orientations and goals. Only a small number of polyprotic acids have been studied in sufficient detail so that all microscopic equilibrium constants can reliably be assigned numbers. Even fewer have been studied with a view to obtaining enough independent data so that assumptions made can be checked for consistency.

Another way to plan a research project is to pick a system that has never been studied carefully, and perform enough preliminary experiments to get some crude data. Then, with these data before you, you can design appropriate experiments that can be interpreted by some chemical model.

It is important that you subject your data and your interpretative model to stringent critical examination. Many of the experimental studies reported in chemical research journals are flawed in this respect. Uses to which computers have been put on preceding pages of this case study are typical of the sorts of quantitative confrontations of model and experiment that can provide convincing objective tests. And you have the tools needed to make such tests.

It is often helpful to think about the data you would expect,

if the tentative model you propose were indeed operative. Computer simulations can be helpful in this regard, allowing you to determine if certain experiments could be helpful, even in principle.

Many sorts of chemical systems can be informative, challenging, or just a little bit different, and can be fun to investigate. You may want to find out what is known about the carbon dioxide—bicarbonate—carbonate equilibria, both in distilled water, and in systems such as blood, or soda pop. You may wish to unravel the multiple equilibria in a polyprotic acid such as EDTA, EGTA, or another of the common complexing agents. Mixtures of acids are important in many ways: can you design a mixture of acids that would make an especially-good buffer over a wide range of pH, or devise a way of titrating two different carboxylic acids in the same solution, obtaining values for the concentration of each? What is the effect on the observed titration behavior of various caids when various metal ions are added to the solutions? How can these effects be explained? Is there ever any difference in the observed equilibrium constants between various optical isomers (the left-hand and right-hand varieties of isomers), or mixtures of both? Or of other kinds of isomers?

Use your imagination, be creative, and show yourself (and maybe your instructor, and perhaps the wider world of other scientists) that you can make some critical, informed, and substantiated judgments about the nature of carboxylic acids in solution.

Appendices

APPENDIX I

PROGRAMING FOR THE PLOTTER

STANDARD FORTRAN STATEMENTS

DRAWING A STRAIGHT LINE: FPLOT(I,X,Y)

The smooth solid curves drawn by the plotter are in fact constructed by instructing the plotter to draw a series of very short straight-line segments. The procedure is to bring the pen to one end of the desired line, with the pen up so that the pen is not writing. The pen is then lowered, and moved while in the down position to the other end of the straight line; a straight line is thereby drawn. An instruction to move to still another position yields a continuation of the line if the pen is down. The necessary information is given to the computer in the form of FPLOT statements of the form

```
CALL FPLOT (I,X,Y)
```

I is an integer controlling the up-down pen position as follows:

I = 0	⇒	no change
I = positive	⇒	control pen before movement
I = negative	⇒	control pen after movement
I = odd	⇒	raise pen
I = even	⇒	lower pen

X and Y are the coordinates of the graph position to which the pen is moved.

PRINTING LABELS ON THE GRAPH

If you want to place labels on the graph, use the FPLOT statement to bring the pen to the position where you wish the

---

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lower left corner of the first character to be. The pen should be in the up position. Then use the statement

```
WRITE(7,J)
```

where J is the number of a format statement of the form

```
J FORMAT('      ')
```

The desired label goes between the ' ' marks.

PLOTTING A POINT ON THE GRAPH

If you wish to plot a point on the graph, you may use the statement

```
CALL POINT(1)
```

This statement cause the plotter to draw an X mark at the current pen position. It expects to find the pen down and it leaves the pen down when finished.

SPECIAL PLOTTING SUBROUTINE

[These subroutines were written by Professor Bruce Hawkins, Department of Physics, Smith College.]

PREPARATION SUBROUTINE: PREP(XS,YS,XO,YO)

This subroutine determines the scale of your graph, sets the position of the origin, and leaves the pen in a convenient position to write a title.

XS is the scale you have chosen for the x-axis, in inches per unit;

YS is the scale you have chosen for the y-axis, in inches per unit;

XO is the distance in inches from the left-hand edge of the graph to the origin;

YO is the distance in inches from the bottom of the graph to the origin.

PREP types a reminder to set the pen position and waits for you to do so. PREP should be called before any other plotting

subroutine. After calling it, a title may be written using an ordinary FORTRAN WRITE statement and its associated FORMAT statement. Since this subroutine uses the typewriter, your IOCS card must mention the typewriter.

A listing of this and each of the other special plotting subroutines appears as the conclusion of this appendix.

SUBROUTINE YAXIS(X,Y,U,N,NLAB)

This subroutine draws the y-axis the length you have chosen, draws evenly-spaced tick marks, places a numerical scale beside the line, and leaves the pen in an appropriate position to write a label for the axis.

X and Y are the coordinates in your own units of the point where the y-axis begins;

U is the distance in your own units between tick marks on the axis;

N is an integer such that N×U is the length of the axis;

NLAB is the number of tick marks which are to be labelled with the value of the scale at the point. NLAB should be equal either to N or to N divided by an integer.

This subroutine should normally be called before the XAXIS subroutine. It leaves the character writing process set to write characters on their side. If you follow this statement with a FORTRAN WRITE statement, you can label the axis.

SUBROUTINE XAXIS(X,Y,U,N,NLAB)

This subroutine behaves exactly like the YAXIS subroutine and like that one can be followed by a WRITE statement to place a label on the axis.

FINISHING THE GRAPH: FINPL

At the end of a graph, or after plotting several graphs on the same axes, it is convenient to use the statement

```
CALL FINPL
```

This subroutine plots a cross at the lower left hand corner of the graph on top of a plus sign put there by PREP. This is a check on machine errors during the plotting. If the two symbols do not land exactly on top of each other, the graph should not be trusted. FINPL then raises the pen and moves it to an appropriate position for beginning a new graph.

NORMS, SAVES, GETS

These three subroutines are listed because they were used within the plotting subroutines.

ON GETTING THE DESIRED GRAPH SIZE

These programs were used with an IBM 1627 x-y strip chart plotter. The system used produced a half-size graph, and so we introduced some factors of 2. into the PREP program. For the standard system, one replaces the statement

```
CALL SCALF (2.*XS,2.*YS,-XO/XS,-YO/YS)
```

with the statement

```
CALL SCALF (XS, YS, -XO/XS, -YO/YS)
```

in the PREP program listed on page 86. The student user is never aware of these considerations.

```
// FOR
*ONE WORD INTEGERS
*LIST SOURCE PROGRAM
      SUBROUTINE PREP (XS,YS,XO,YO)
C     SETS SCALE, ORIGIN, AND LOCATES PEN TO WRITE A TITLE
C     IT PLOTS A REGISTER POINT AT THE INITIAL POSITION OF THE PEN AND
C     IT ADJUSTS THE SCALE TO THE HALF SIZE STEPS OF THIS PLOTTER
C     XS, YS ARE X AND Y SCALES IN INCHES PER USER'S UNIT AND MUST BE
C          VARIABLES SINCE PREP CHANGES THEM
C     PREP ASSUMES THAT THE PEN IS AT THE LOWER LEFT HAND CORNER OF
C          THE GRAPH
C     XO IS THE DISTANCE IN INCHES FROM THE LEFT HAND SIDE OF THE
C          GRAPH TO THE ORIGIN
C     YO IS THE DISTANCE IN INCHES FROM THE BOTTOM OF THE GRAPH TO THE
C          ORIGIN
C
      IF (NSW-16324) 6,10,6
    6 WRITE (1,1)
    1 FORMAT('PLACE PEN AT RIGHT EDGE OF PLOTTER AND PUSH START')
      PAUSE
      CALL SAVES (XS,YS,XO,YO)
   10 CALL SCALF (1.,1.,0.,0.)
          CALL FPLOT (-2,-.15,.05)
      DO 5 I=1,20
      CALL FPLOT(0,-.15,.15)
      CALL FPLOT (0,-.05,.15)
      CALL FPLOT (0,-.05,.05)
    5 CALL FPLOT (0,-.15,.05)
          CALL FPLOT (1,0.,0.)
      CALL FPLOT (-2,0.,.2)
      CALL POINT (0)
      CALL SCALF (2.*XS,2.*YS,-XO/XS,-YO/YS)
      CALL FCHAR ( (1.-XO)/XS,(10.-YO)/YS,.2,.4,0.)
      NSW = 16324
      RETURN
      END
// DUP
*STORE      WS  UA  PREP
```

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```
// FOR
*ONE WORD INTEGERS
*LIST SOURCE PROGRAM
      SUBROUTINE YAXIS (X,Y,U,N,NLAB)
C     PUTS A STANDARD YAXIS ON PLOT STARTING AT X,Y, WITH N SEGMENTS
C     OF LENGTH U SEPARATED BY TICK MARKS AND LABELS NLAB +1 OF THE
C     TICKS WITH THE SCALE VALUE AT THAT POINT, X AND Y ARE IN USERS
C     UNITS AS DEFINED BY XS AND YS WHICH ARE INCHES/ USER'S UNIT
C     MUST BE PRECEEDED BY A CALL TO PREP OR SCALF
C     LEAVES PEN POSITIONED FOR LEGEND
C
      CALL GETS (XS,YS,XO,YO)
      CALL FGRID (1,X,Y,U,N)
      CALL FCHAR (X, Y, .2,.3,1.570795)
           IE = NLAB + 1
           TENLG = .4342945*ALOG(Y+U*FLOAT(N))
             DO 5 I=1,IE
             YP = Y+U*FLOAT((I-1)*(N/NLAB))
             CALL FPLOT (0,X-.1/XS,YP-.5/YS)
                IF (ABS(YP*YS)-.05) 4,4,6
    4              WRITE (7,10)
   10               FORMAT (5X,'0')
                  GO TO 5
    6 CALL NORMS (TENLG,YP)
    5 CONTINUE
      CALL FPLOT (0,X-.3/XS,Y+(U*FLOAT(N))/4.)
      RETURN
      END
// DUP
*STORE       WS  UA  YAXIS
```

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```
// FOR
*ONE WORD INTEGERS
*LIST SOURCE PROGRAM
      SUBROUTINE XAXIS     (X,Y,U,N,NLAB)
C     PUTS A STANDARD XAXIS ON PLOT STARTING AT X,Y, WITH N SEGMENTS
C     OF LENGTH U SEPARATED BY TICK MARKS AND LABELS NLAB +1 OF THE
C     TICKS WITH THE SCALE VALUE AT THAT POINT, X AND Y ARE IN USERS
C     UNITS AS DEFINED BY XS AND YS WHICH ARE INCHES/ USER'S UNIT
C     MUST BE PRECEEDED BY A CALL TO PREP OR SCALE
C     LEAVES PEN POSITIONED FOR LEGEND
C
      CALL GETS(XS,YS,XO,YO)
      CALL FGRID(0,X,Y,U,N)
      CALL FCHAR (X, Y, .2,.3,0.)
           IE = NLAB+1
           TENLG =  .4342945*ALOG(X+U*FLOAT(N))
             DO 5 I= 1,IE
             XP = X+U*FLOAT((I-1)*(N/NLAB))
      CALL FPLOT (0,XP-.5/XS,Y-.25/YS)
                 IF (ABS(XP*XS)-.05) 4,4,6
    4 WRITE (7,10)
   10 FORMAT (5X,'0')
                 GO TO 5
    6            CALL NORMS (TENLG,XP)
    5 CONTINUE
      CALL FPLOT (0,X+(U*FLOAT(N))/4.,Y-.5/YS)
      RETURN
      END
// DUP
*STORE       WS  UA  XAXIS
```

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```
// FOR
*ONE WORD INTEGERS
*LIST SOURCE PROGRAM
      SUBROUTINE FINPL
C     FINPL PLOTS A REGISTER POINT IN TOP OF THE ONE MADE BY PREP AND
C     MOVES THE PEN TO BLANK PAPER (ASSUMING AN 8.5 BY 11 GRAPH).
C
      CALL GETS (XS,YS,XO,YO)
      X=-XO/XS
      Y=-YO/YS
      CALL FPLOT (1,X,Y)
      CALL FPLOT (-2,X,Y)
      CALL POINT (1)
      CALL FPLOT (1,9./XS+X,Y-.2/YS)
      RETURN
      END
// DUP
*STORE      WS  UA  FINPL
```

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```
// FOR
*ONE WORD INTEGERS
      SUBROUTINE NORMS (TENLG,P)
C     WRITES SCALES ON AXES ADJUSTING THE FORMAT TO THE SIZE OF THE
C           SCALE
C
      NPOW = IFIX (TENLG+.01)
      P = P+SIGN (.00005*(10.**NPOW),P)
      IF (TENLG-3.4) 5,5,30
    5 IF (TENLG+2. ) 30,6,6
    6 NPOW = NPOW + 3
      NP=P
      GO TO (11,12,13,14,15,16),NPOW
   11       WRITE (7,21) P
   21       FORMAT (F7.4)
            GO TO 50
   12     WRITE (7,21) P
          GO TO 50
   13       WRITE (7,23) P
   23       FORMAT (F6.3)
            GO TO 50
   14     WRITE (7,24) P
   24     FORMAT(F6.2)
          GO TO 50
   15       WRITE (7,25) P
   25       FORMAT (F6.1)
            GO TO 50
   16     WRITE (7,26) NP
   26     FORMAT (I5)
          GO TO 50
   30 WRITE (7,35) P
   35 FORMAT (E10.3)
   50 RETURN
      END
// DUP
*STORE       WS  UA  NORMS
```

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```
// ASM   SAVES AND GETS ROUTINE TO STORE SCALE AND ZERO FOR PLOT ROUTINES
*LIST
                    ENT     SAVES
                    ENT     GETS
XS      DEC         1.      DEFAULT VALUES
YS      DEC         1.      DEFAULT VALUES
XO      DEC         0.
YO      DEC         0.
SAVES   DC          *-*
        STX   1     SVX1+1
        STX   2     SVX1+3
        LDX   I1    SAVES   GET PARAM ADDR
        MDX   1     4       FOR INDEXED PICK-UP
        STX   1     SVLP+1
        STX   1     SVOUT+1 IS ALSO EXIT ADDRESS
        LDX   1     -4      FOR PICK UP LOOP
        LDX   2     0
SVLP    LDD   I1    *-*     FILLED BY END OF PARAM ADDR
        STD   L2    XS
        MDX   2     2
        MDX   1     1
        MDX         SVLP
SVX1    LDX   L1    *-*
        LDX   L2    *-*
SVOUT   BSC   L     *-*     EXIT ADDRESS SUPPLIED
GETS    DC          *-*
        STX   1     GTX1+1
        STX   2     GTX1+3
        LDX   I1    GETS
        MDX   1     4       LIKE SAVE PROCEEDURE
        STX   1     GTPR+1
        STX   1     GTOUT+1
        LDX   1     -4
        LDX   2     0
GTLP    LDD   L2    XS
GTPR    STD   I1    *-*     DESTINATION ADDR FILLED IN
        MDX   2     2
        MDX   1     1
        MDX         GTLP
GTX1    LDX   L1    *-*
        LDX   L2    *-*
GTOUT   BSC   L     *-*     EXIT ADDRESS SUPPLIED
        END
```

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APPENDIX II

NATIONAL BUREAU OF STANDARDS BUFFERS FOR CALIBRATING A pH METER

Before using a pH meter for measurement of pH, the meter must be calibrated using a solution of accurately-known pH. The information in this appendix, giving instructions for preparing such standard solutions and the pH values of those solutions, is taken from the following publications of the United States National Bureau of Standards:

¶Potassium Tetroxalate (pH = 1.679 at 25°C), N.B.S. Certificate for Standard Sample 189, January 10, 1964.

¶Potassium Hydrogen Tartrate (pH = 3.557 [saturated solution], pH = 3.639 [0.01 molal solution] at 25°C), N.B.S. Certificate for Standard Sample 188, January 10, 1964.

¶Potassium Hydrogen Tartrate (pH = 4.008 at 25°C), N.B.S. Certificate for Standard Reference Material 185d, July 21, 1966.

¶Potassium Dihydrogen Phosphate and Disodium Hydrogen Phosphate, equi-molal mixture (pH = 6.862 at 25°C), N.B.S. Certificate for Standard Reference Materials 186-I-c and 186-II-b, May 1, 1969.

¶Borax (pH = 9.180 at 25°C), N.B.S. Certificate for Standard Sample 187a, January 10, 1964.

For highest accuracy, N.B.S. Standard Reference Materials should be used and the directions followed exactly. Comparable reagents and comparable procedures will give satisfactory results for pH equipment which can be read to ±0.01 pH units, since the greater precision of the N.B.S. values is not needed.

POTASSIUM TETROXALATE A 0.05-molal solution of potassium tetroxalate dihydrate is recommended by use as a pH standard. To prepare the solution, weigh 1.261 grams of the salt into a 100-mℓ

volumetric flask. Dissolve the salt and fill to the mark with distilled water. The salt should not be dried before weighing. Values of the pH of this solution at various temperatures are given in the following table:

°C	pH	°C	pH	°C	pH
0	1.666	30	1.683	55	1.715
5	1.668	35	1.688	60	1.723
10	1.670	38	1.691	70	1.743
15	1.672	40	1.694	80	1.766
20	1.675	45	1.700	90	1.792
25	1.679	50	1.707	95	1.806

The uncertainty of these values is estimated not to exceed ±0.005 pH units for temperatures from 0 to 60°C and ±0.01 units from 60 to 95°C. The liquid-junction potential of the common pH cell displays a considerably greater cariability in solutions of less than 2.5 than in solutions of pH between 2.5 and 11.5. For this reason, experimental pH values may differ by as much as 0.02 to 0.05 pH units from the values given above.

POTASSIUM HYDROGEN TARTRATE A solution saturated with potassium tartrate near 25°C is recommended as a standard for the calibration of pH equipment at temperatures between 25 and 95°C. A 0.01-molal solution is also recommended as a pH standard for the temperature range from 0 to 60°C.

The saturated solution is prepared by adding an excess of the salt to distilled water contained in a glass-stoppered bottle or flask. Then shake vigorously. With a 100 percent excess of the salt, a few minutes of shaking is sufficient for saturation.

One hundred mℓ of water will dissolve about 0.7 g of the salt at 25°C. Allow the solid to settle and decant the clear solution, or filter if necessary. Store the solution in a glass-stoppered Pyrex or Kimax bottle. For an accuracy of ±0.001 pH units, the temperature of saturation must lie between 24 and 26°C.

To prepare the 0.01-molal solution, weigh 0.1878 grams of the salt to a 100-mℓ volumetric flask. Fill to the mark with distilled water having a conductivity not exceeding 2×10^{-6} $ohm^{-1}cm^{-1}$ at 25°C. The salt need not be dried before use. Shake well.

These tartrate solutions are very susceptible to mold growth which is usually accompanied by an increase of a few hundredths in the pH value. For the most accurate results, tartrate standards should be prepared fresh each day. If they must be kept longer, they should be stored in a refrigerator.

Values of the pH of the saturated solution are given in the following table. It is assumed that the temperature of saturation is in each case 25°C, and that the temperature of measurement of pH is the temperature listed in the table.

°C	pH	°C	pH	°C	pH
25	3.557	45	3.547	70	3.580
30	3.552	50	3.549	80	3.609
35	3.549	55	3.554	90	3.650
38	3.548	60	3.560	95	3.674
40	3.547				

The uncertainty of these pH values is estimated not to exceed ±0.005 pH units from 25 to 60°C, and ±0.01 units from 70 to 95°C.

Values of the pH of the 0.01-molal solution at various

temperatures are given in the following table:

°C	pH	°C	pH	°C	pH
		20	3.647	40	3.632
0	3.711	25	3.639	45	3.635
5	3.689	30	3.635	50	3.639
10	3.671	35	3.632	55	3.644
15	3.657	38	3.631	60	3.651

The uncertainty in these pH values is estimated not to exceed ±0.005 pH units.

POTASSIUM HYDROGEN PHTHALATE A 0.05-molal solution of potassium hydrogen phthalate is recommended for the standardization of pH equipment. The salt should meet the specifications of the American Chemical Society for reagent grade chemical, and should be dried for 2 hours at 110°C before use. To prepare the solution, weigh 1.012 grams of the dried salt into a 100-mℓ volumetric flask. Add sufficient distilled water to dissolve the salt, and then fill to the mark with distilled water. Mix the solution thoroughly by shaking. The distilled water should have a conductivity not exceeding 2×10^{-6} $ohm^{-1}cm^{-1}$. The solution should be protected against evaporation and contamination by molds. It should be discarded if mold growth occurs. Values of the pH of this standard solution at various temperatures are:

°C	pH	°C	pH	°C	pH
0	4.012	30	4.014	60	4.089
5	4.005	35	4.023	70	4.12
10	4.002	40	4.033	80	4.16
15	4.001	45	4.045	90	4.20
20	4.003	50	4.058	95	4.22
25	4.008	55	4.073		

The uncertainty of these pH values is estimated not to exceed ±0.005 pH units for temperatures from 0 to 60°C, and ±0.01 unit from 70 to 95°C.

PHOSPHATE MIXTURE A 0.05-molal phosphate solution (0.025 molal with respect to both KH_2PO_4 and Na_2HPO_4) is recommended for the calibration of pH equipment. Both salts should meet the specifications of the American Chemical Society for reagent grade chemicals, and should be dried for 2 hours at 110 to 130°C before use. To prepare the solution, weigh 0.3388 grams of the dried potassium dihydrogen phosphate and 0.3533 grams of the dried disodium hydrogen phosphate into a 100-mℓ volumetric flask. Dissolve the salt and then fill to the mark with carbon-dioxide-free distilled water. The water can be freed from carbon dioxide by boiling distilled water for 10 minutes and guarding it with a soda-lime tube while cooling. The distilled water should have a conductivity no greater than 2×10^{-6} $ohm^{-1}cm^{-1}$. Although elaborate precautions to prevent contamination of the buffer solution with atmospheric carbon dioxide are usually unnecessary, the container should be kept tightly stoppered at all times when a sample is not actually being removed. The solution should be replaced after a few weeks, or sooner if molds or sediment appear, or if it has been exposed repeatedly to air containing carbon dioxide.

°C	pH	°C	pH	°C	pH
0	6.981	30	6.850	55	6.832
5	6.948	35	6.841	60	6.836
10	6.920	38	6.837	70	6.845
15	6.897	40	6.835	80	6.859
20	6.878	45	6.831	90	6.877
25	6.862	50	6.830	95	6.886

The uncertainties in the pH values listed in the preceding table are estimated not to exceed ±0.005 pH units from 0 to 60°C and ±0.01 units from 70 to 95°C. Minor variations of the order of a few thousandths of a pH unit may be expected to occur between different lots of phosphate salts.

BORAX A 0.01-molal solution prepared from $Na_2B_4O_7 \cdot 10H_2O$ is recommended for the calibration of pH equipment. The salt should meet the specifications of the American Chemical Society for reagent grade chemical. The water content of this salt, stored under ordinary conditions, is less than indicated by the formula. This does not affect the use of the salt as a pH standard. However, the salt must not be dried in an oven before use. To prepare the solution, crush gently any large lumps of the salt, and weigh 0.380 grams into a 100-mℓ volumetric flask. Dissolve and then dilute to the mark with carbon-dioxide-free distilled water. The water can be freed from carbon dioxide by boiling distilled water for 10 minutes and guarding it with a soda-lime tube while cooling. The distilled water should have a conductivity no greater than 2×10^{-6} $ohm^{-1}cm^{-1}$. To avoid contamination of the buffer solution with atmospheric carbon dioxide, keep the stopper in place except when removing a portion of the solution. If desired, the solution may be protected with a soda-lime tube.

°C	pH	°C	pH	°C	pH
0	9.464	30	9.139	55	8.985
5	9.395	35	9.102	60	8.962
10	9.332	38	9.081	70	8.921
15	9.276	40	9.068	80	8.885
20	9.225	45	9.038	90	8.850
25	9.180	50	9.011	95	8.833

The uncertainties in the pH values listed in the preceding table for standard borax buffer solutions have uncertainties estimated not to exceed ±0.005 pH units from 0 to 60°C, and ±0.01 units from 70 to 95°C.